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REVISION OF THE ATOMIC WEIGHT OF ALUMINUM.[1]

BY J. W. MALLET, F. R. S.,

Professor of Chemistry in the University of Virginia.

Need for a Re-determination of the Atomic Weight of Aluminum.

There is probably no one of the so-called chemical elements equally abundant in nature with aluminum, and occurring in as numerous compounds, with regard to the atomic weight of which our knowledge has long rested upon so slender a foundation of accurate experiment. The following brief statement includes, I believe, all the determinations of this constant which are on record.

Former Determinations.

1. *Experiments of* BERZELIUS, 1812.—Berzelius[2] precipitated a solution of alum by addition of ammonia, dissolved the precipitate in sulphuric acid to saturation, filtered, concentrated the filtrate by evaporation, and threw down aluminum sulphate by alcohol. This salt was well washed with alcohol, to separate as far as possible any excess of acid, and was then heated in a platinum crucible over an alcohol lamp, weighing from time to time, until

[1] From the Philosophical Transactions of 1880. Paper read before the Royal Society, April 22, 1880.

[2] Gilbert's Annalen der Physik, 40 (1812), 260.

no further loss of weight occurred. The anhydrous sulphate so obtained was but slowly soluble in water on heating, but left no insoluble residue. 10 grams of this salt was now raised to a higher temperature in a weighed platinum crucible, and strongly heated as long as any loss of weight could be detected. The residue of loose, light, white alumina found in the crucible weighed 2.9934 grams. Consequently the salt consisted of—

"Sulphuric acid" (SO_3)	70.066	or	100.000
Alumina	29.934	or	42.722
	100.000	or	142.722

Several small arithmetical errors have been made in the discussion of this single experiment of Berzelius, upon which for nearly half a century the value assigned to the atomic weight of aluminum may be said to have rested.

In the original paper it is calculated that if 42.722 parts of alumina contain 19.96 parts of oxygen (the atomic weight of sulphur being then taken $=201.16$—$O=100$), 100 parts of alumina must include 46.726 parts of oxygen. This last number should be 46.7207. In a later paper[1] by the same author, it is calculated from the results of the above experiment, that 100 parts of "sulphuric acid" are saturated by 42.7227 parts of alumina, and that the earth contains 46.7047 per cent. of oxygen; the earth is assumed to be Al_2O_3, and consequently the atomic weight of Al is found $=171.667$ ($O=100$), or 27.49 ($H=1$). These numbers, correctly calculated from the percentage of oxygen taken in this second paper, should read 171.167 and 27.39 respectively. Or, if the percentage of oxygen of the former paper, corrected as above, be taken as 46.7207, the atomic weight, for Al_2O_3, will be 171.057 ($O=100$) or 27.37 ($H=1$).[2]

Finally, if Berzelius' direct results of experiment be taken, and recalculated with Stas' atomic weights for O (15.96) and S (31.98), the atomic weight of aluminum, its oxide being assumed Al_2O_3, will be 27.237 in reference to that of hydrogen as unity.

Berzelius[3] also attempted to obtain a pure hydrate of aluminum by precipitating the sulphate and nitrate with ammonia, but found

[1] Poggendorff's Annalen der Physik u. Chimie, 8 (1826), 187.

[2] A. C. Oudemans, Jr. (in his Historisch-kritisch Overzigt van de Bepaling der Æquivalent-Gewigten van twee en twintig Metalen; Leiden, 1853), calculates, from Berzelius' figures, $Al=171.02$.

[3] Gilbert's Annalen, *loc. cit.*

that highly basic salts only were thrown down. Using the chloride instead, a hydrate was obtained which, after being dried in the sun, gave only water on heating, but there was a little loss from mechanically-carried-over alumina. This sun-dried hydrate left 64.932 per cent. of alumina free from acid. Berzelius therefore calculates that 100 parts of anhydrous alumina had been combined with 54 parts of water—this amount of water containing 47.65 parts of oxygen; while the alumina contains, as shown by the above-quoted analysis of the sulphate, 46.726 parts of oxygen. He remarks: "I cannot affirm that either the determination of the amount of water or that of the oxygen in the alumina is sufficiently exact; both are, however, so far so as to sufficiently show us that alumina, like the preceding bases, combines with an amount of water whose oxygen is equal to that of the earth itself."

In the decomposition by heat of aluminum sulphate, as thus used to furnish data from which to calculate the atomic weight of the metal, the following possible sources of error may be noticed: The hydrate precipitated by ammonia from a solution of (presumably) *potash* alum might carry down with it traces of fixed alkali, and this latter be retained in the sulphate afterwards prepared from the hydrate. The tendency of aluminum to form basic salts suggests the possibility of traces of sulphuric acid being lost in the preliminary drying over the simple alcohol lamp, even at a temperature at which possibly the last traces of water might not have been removed. I have found from my own experiments that a trace of basic sulphate may, on the other hand, be obstinately retained even after prolonged exposure to a very high temperature, when it might be assumed that pure alumina alone was left. As Berzelius himself says, ignited alumina rapidly absorbs moisture from the air, involving risk of error in determining its weight. Traces of the light pulverulent alumina are liable to be mechanically carried away during the decomposition of the sulphate. It is observable that all these sources of error, except the last, tend in the same direction, to make the atomic weight of aluminum come out too high.

2. *Experiments of* Sir HUMPHRY DAVY, 1812.—In Sir Humphry Davy's "Elements of Chemical Philosophy"—published in 1812, the same year in which Berzelius' first paper on this subject appeared—it is stated[1] that no direct researches had then been made

[1]Vol. 4, 263, of the Collected Works of Sir H. Davy, edited by his brother Dr. John Davy London, 1840.

on the quantity of oxygen in alumina, but that, from some experiments by the author on the quantity of ammonia required to decompose saturated solutions of alumina in acids, "it would appear that the number representing alumina is about 48, and, supposing it to consist of one proportion of aluminum and one of oxygen, 33 will be the number representing aluminum." The details of the experiments in question are not given, and the combining proportions of all substances having been very imperfectly known at the time—the number 15 is taken above for oxygen—it is needless to say that this passage throws no light upon the exact atomic weight of aluminum.

3. *Experiments of* THOMSON, 1825.—Thomson[1] attempted to deduce the number representing this atomic weight from, (*a*) analyses by himself and others of sundry natural aluminous silicates, (*b*) analyses of potassium alum, and (*c*) analyses of hydrates of aluminum. He concluded from all his experiments that the true number for alumina is 2.25 ($O=1$), and, taking alumina to be AlO, he made $Al=1.25$. This corresponds to $Al=30$, if O be assumed $=16$, and alumina Al_2O_3—a result which can only be viewed as a rough approximation to the truth, since Thomson's methods were far from accurate, and his experimental results agree but poorly with each other.

4. *Experiments of* MATHER, 1835.—W. W. Mather,[2] Assistant Professor of Chemistry at the United States' Military Academy, West Point, prepared anhydrous aluminum chloride by Wöhler's process, dissolved a weighed portion of it in water, added silver nitrate in excess, filtered off, dried and weighed the silver chloride formed, threw down excess of silver from the filtrate by hydrochloric acid, filtered again, evaporated this second filtrate and washings to dryness, ignited the residue, and weighed it as alumina. .646 gram of aluminum chloride gave 2.0549731[3] grams of silver chloride (yielding on reduction 1.548161 gram of silver) and .2975 gram of alumina.

From the amount of silver chloride found and silver obtained from it in this one experiment, and from the atomic weights of silver and chlorine adopted by Berzelius and Thomson respectively,

[1]Thomas Thomson, M.D., An Attempt to Establish the First Principles of Chemistry by Experiment, **1**, 285; London, 1825.

[2]Silliman's American Journal of Science and Arts, **27** (1835), 241.

[3]The seven decimal places are given, notwithstanding the statement by the author himself that his balance could weigh easily $\frac{1}{300}$ grain, and was sensible to $\frac{1}{700}$ grain!

Mather calculated values for the atomic weight of aluminum ranging from 1.82274 to 1.85430 ($O=1$, and the formula of the chloride being taken as $AlCl_3$), or 29 16384 to 29.66880 for $O=16$; but from the amount of alumina obtained and the amount of aluminum therein (the latter deduced from the chloride taken for analysis minus the chlorine found), he calculated the atomic weight for aluminum as 1.3188017 ($O=1$) for alumina taken as Al_2O_3, or 21.1008272 for $O=16$. He does not seem to have been struck by the evidence of some error in his own work which these discrepant numbers afford, but suggested that the figures given by Berzelius for the aluminum and oxygen in alumina might have been accidentally inverted, which would explain the disagreement between himself and the great Swedish chemist. In reality it is pretty plain that Mather's alumina was not pure, either from fixed matter of some kind left behind from the acids and wash water used, or from absorption of moisture before weighing. If his most direct result only be taken as the basis of calculation, namely, the weight of aluminum chloride used and silver chloride obtained from it, using Stas' numbers for chlorine (35.37) and silver (107.66), the atomic weight of aluminum found will be 28.778 for the formula $AlCl_3$.

5. *Experiments of* MALLET, 1857.—In 1857 the writer of this paper attempted to use metallic aluminum, which had not long before begun to be manufactured and sold, for the determination of the atomic weight. At the meeting of the British Association held in that year at Dublin,[1] he gave a brief account of his experiments, which had been made with the metal of commerce, containing, as he found, only from 93 to 96 per cent. of pure aluminum. The exact nature and amount of the foreign substances present, chiefly iron and silicon, having been determined, the crude metal was dissolved in hydrochloric acid, the solution precipitated by ammonia, and from the amount of alumina left from the precipitate on ignition, after allowing for the impurities, the atomic weight was deduced. The results obtained from a few experiments were not satisfactory enough to warrant any proposal to modify the then received number. The probability that this number needed correction was, however, pointed out, with reasons for such an opinion; the desirability of obtaining for the purpose of new experiments really pure metallic aluminum was noticed; and it was suggested that

[1] Report of British Association Meeting at Dublin, 1857; Transactions of Sections, 53.

difficulties connected with the accurate determination of alumina by the method which had just been tried might make it eligible to determine instead the hydrogen given off during the solution of the metal in acid.

6. *Experiments of* DUMAS, 1858.—Dumas[1] redetermined the atomic weight in question by dissolving in water known weights of aluminum chloride, and ascertaining the quantity of silver, used as nitrate, which was required in each case for precipitation of the chlorine. The aluminum chloride had been carefully prepared on the large scale, then sublimed from iron turnings, and resublimed from aluminum filings. It sometimes still contained traces of iron. Each specimen to be used was sublimed for the last time from aluminum, in a stream of dry hydrogen, into a small glass tube, which was sealed at both ends before the lamp, and reserved for one of the analytical experiments. Of these there were seven. In each the weight of the sealed tube and its contents was taken, a drawn out end opened, and the weight quickly verified after equilibrium of pressure with the outside air had been thus established; the tube was introduced into water, and after solution of its contents the weight of the empty tube was determined. It does not appear from the published paper how the risk of mechanical loss from violent action of the chloride on the water was guarded against; from my own experiments with the bromide this appears to be a point requiring careful attention. Nor is it stated how the quantity of silver used was determined, whether by weighing the chloride of silver formed, by measuring the volume of a standard solution of silver nitrate, or by weighing off a little less metallic silver than would be required, converting this into nitrate, adding it to the aluminum chloride solution, and completing the precipitation with a measured quantity of dilute standard solution of silver nitrate. Nor is it mentioned how, if at all, the error due to slight solubility of silver chloride in the liquid from which it was precipitated is obviated—a point not ignored by Dumas, as appears from another part of the same paper,[2] and afterwards very carefully examined by Stas.

The results of the seven experiments were as follows, the atomic weight or equivalent being calculated for the formula Al_2Cl_3, and on the supposition that $Ag=108$, and $Cl=35.5$:—

[1] Annales de Chimie et de Physique [3], **55** (1859), 151. [2] Page 135.

					Atomic Weight.
I.—1.8786	of Al_2Cl_3 required	4.543	of Ag	=13.74	
II.—3.021[1]	" "	7.292	"	=13.85	(should be 13.86)
III.—2.399	" "	5.802	"	=13.73	
IV.—1.922	" "	4.6525	"	=13.68	
V.—1.697	" "	4.1015	"	=13.77	
VI.—4.3165	" "	10.448	"	=13.68	
VII.—6.728	" "	16.265	"	=13.76	
	Mean			13.744	
	Should be			13.746	or 27.492 for $AlCl_3$

Recalculating this table for the formula $AlCl_3$, and using the atomic weights of Stas for silver (107.66) and chlorine (35.37), the figures of the last column become—

I.	Atomic weight of Al	=27.447
II.	" " "	=27.696
III.	" " "	=27.435
IV.	" " "	=27.318
V.	" " "	=27.522
VI.	" " "	=27.327
VII.	" " "	=27.489
	Mean	27.462

It is to be remarked that the tendency of the chief causes of error connected with these experiments is in the same general direction. The presence of any iron in the chloride used; the action upon it, though but to a minute extent, of any trace of moisture in the hydrogen in which it was finally sublimed; any loss occurring with the fumes formed on introduction of the chloride into water; and the retention of traces of silver chloride in solution in the liquid from which the main mass of this compound had been thrown down; any or all of these would tend to diminish the quantity of silver chloride obtained, and therefore to make the atomic weight of aluminum appear greater than it really is. In discussing results which we owe to the labors of such experimenters as Berzelius and Dumas, it is of course to sources of error likely to inhere in the method itself that attention should especially be given.

Dumas also tried dissolving aluminum (containing iron and silicon in considerable quantity) in hydrochloric acid, adding nitric

[1] Contained traces of iron.

acid in excess, evaporating to dryness, igniting and weighing the alumina (and other oxides) left behind. From an analysis of the crude metal employed, so as to allow for the impurities present, and on the basis of three experiments made as above, he calculated the atomic weight as

13.74	(=27.48	for Al_2O_3—$O=16$)
13.87	(=27.74	" " — ")
13.89	(=27.78	" " — ")

but he was dissatisfied with these results, having found that the impurities of the metallic aluminum were unequally distributed throughout its mass, and having been unable to obtain the metal in a pure state. He considered the results furnished by the experiments with the chloride as accurate, and concluded that the atomic weight of Al is represented by the number 13.75 (for Al_2Cl_3)—this becomes 27.5 for $AlCl_3$ or Al_2Cl_6.

7. *Experiments of* TISSIER, 1858.—Ch. Tissier[1] prepared aluminum by reducing very pure fluoride of aluminum and sodium —probably cryolite, although this is not stated—by means of purified sodium in a carbon crucible, re-fusing the metal several times in order to free it from any of the flux which might have been retained. No account is given of the means taken to prepare a carbon crucible free from iron and silicon; and to prevent destruction of the crucible by its material burning away during the fusion at high temperature of the aluminum salt with sodium. The metal was tested for iron by dissolving it in nitro-hydrochloric acid, evaporating to dryness with a large excess of nitric acid, and igniting the residue of alumina, which was observed to be of brilliant whiteness, while the addition of a solution containing a few thousandths of iron sufficed "to color it very strongly red." Why the much more delicate tests available for iron in the original solution were not used does not appear.

As regards silicon, it is stated that "the solution of the metal by means of hydrochloric acid left no trace of silicon"; no mention is made of the solution having been evaporated to dryness, the residue remoistened with strong hydrochloric acid and dissolved in water in order to see whether silica was left. A portion of the solution obtained with nitro-hydrochloric acid was evaporated to dryness, the residue ignited, and the alumina so left was digested

[1] Comptes Rendus des Séances de l'Acad. des Sciences, **46** (1858), 1105.

with a strong and boiling solution of ammonium nitrate. This solution was evaporated to dryness, and left a residue of sodium nitrate representing 0.135 per cent. of sodium in the metallic aluminum.

1.935 gram of this aluminum was dissolved in hydrochloric acid, the solution evaporated with an excess of nitric acid until all chlorine was completely driven off, and the residue heated until the nitric acid was also completely removed and alumina only was left. This alumina weighed 3.645 grams. In the paper recording this single experiment the resulting atomic weight is not calculated, but the author simply points out that the number 14, which he says many chemists adopt as representing aluminum, must be too high, while 13.75, the number assigned by Dumas, is in all probability accurate. In support of this view it is calculated that, if $Al = 14$, the alumina obtained in the above described experiment should have weighed 3.590[1] grams; whereas, with $Al = 13.75$, its weight should have been 3.624 grams. In getting these figures O is taken $= 8$.

But, if the minute quantity of sodium stated to have existed in the metal used be deducted, and allowed for as sodium oxide (aluminate) in the last weighed residue, and if the results obtained be calculated, for alumina $= Al_2O_3$, with Stas' number for oxygen (15.96), the atomic weight of aluminum will be represented by 27.068, a number much nearer to 27 than to 27.5 (13.75×2), the value assumed as most probably correct by Tissier.[2]

8. *Experiments of* TERREIL, 1879.—Lastly, about a year ago Terreil[3] made a determination of the constant in question by passing hydrochloric acid gas over metallic aluminum, collecting and measuring the hydrogen evolved. He placed a known weight of aluminum in a tube of hard glass, the tube wrapped with foil so as to allow of its being made red hot. By one end a stream of well dried gaseous hydrochloric acid could be introduced, while a smaller tube extended from the other end and dipped into a vessel of water.

[1] This ought to read 3.594.

[2] Since this paper was printed in the Philosophical Transactions my attention has been drawn by Prof. F. W. Clarke of Cincinnati to a single other determination made in 1868 by Isnard (Comptes rendus, **66**, 508). The report of this is very brief and without any satisfactory details, the whole of it being the following lines: "The process employed by the author consists in attacking the metal by hydrochloric acid. He finds that 9 grams of aluminum, attacked by pure hydrochloric acid, invariably give, after calcination, 17 grams of alumina; whence he concludes that 9 would represent the equivalent of aluminum as referred to hydrogen taken as unity."

[3] Bulletin de la Société Chimique de Paris, **31** (20 Fév. 1879), 153.

The air was first expelled from the apparatus by a current of dry carbon dioxide, and not until the gas passing through was capable of being completely absorbed by a solution of potash was the hydrochloric acid introduced, this latter itself freed from atmospheric air. The gas escaping from the tube was now collected in a graduated jar, and the temperature of the tube containing the aluminum was raised to a red heat. As soon as hydrogen ceased to come over, the gas in the jar was shaken up with potash to absorb any carbon dioxide which it might contain, and the volume was measured, and reduced by calculation to its equivalent under normal temperature and pressure. The aluminum chloride left in the tube was pulverulent and snow white.

No details are given of the method by which pure metallic aluminum was prepared, although this has been the great difficulty in the way of obtaining accurate results from experiments made with the metal as the starting point, nor is there any record of the tests applied to prove the purity of the metal used. The gas was collected over water, in which hydrogen is not altogether insoluble, and from which more or less of the gases of atmospheric air would be given off into the hydrogen. Nothing is said of the vapor of water, mixed with the hydrogen in proportion depending upon the temperature, having been removed, or its amount calculated and allowed for; though as it is not likely that so obvious a precaution was neglected, it may be supposed that the potash spoken of as used to absorb any carbon dioxide left was either solid hydrate or so strong a solution as to have also removed most if not all the aqueous vapor.

The results of the single experiment reported were—

Weight of aluminum	.410 gram.
Volume of hydrogen collected at 11° and 768 mm. . .	530 cc.
Corresponding volume at normal temperature and pressure	508.2 cc.
Weight of this hydrogen	.0455 gram.

from which the author calculates

$$.0455 : .4100 = 1 : 9.01,$$

giving the atomic weight 13.515 (for Al_2Cl_3) or 27.03 (for $AlCl_3$).

In verifying the above calculation I have found as the result of reducing the volume of hydrogen from the given to normal temperature and pressure 514.85 cc. instead of 508.2 cc., but this, I am satisfied, arises from the number representing the pressure at

the time of experiment being, doubtless by a printer's error, wrongly given as 768 instead of 758 mm. With the latter figures the result is as recorded in the paper, and of course such atmospheric pressure is more frequently observed than that which appears in the above table.

It is pretty plain that from the researches which have been quoted we may reject those of Davy, Thomson, and Mather as incapable of giving exact results, this being either admitted by the authors themselves or shown by an examination of their methods and the inconsistency of their conclusions. Our knowledge of the atomic weight under consideration rests therefore upon the investigations of Berzelius, Tissier, and Terreil, each of whom made one experiment, and those of Dumas, who made seven.

General results of former determinations.—If all the results be taken as I have re-calculated them, using Stas' atomic weights for the other elements concerned, and equal value be given to all, we shall have the following arithmetic mean—

Berzelius	27.237
Dumas	27.447
"	27.696
"	27.435
"	27.318
"	27.522
"	27.327
"	27.489
Tissier	27.068
Terreil	27.030
Mean	27.357

If, however, the results of Dumas, all depending on repetition of the same process, be viewed as possibly affected by some constant error, and be thrown together, taking into the calculation the mean only of his seven experiments, the general mean will be—

Berzelius	27.237
Dumas (mean)	27.462
Tissier	27.068
Terreil	27.030
Mean	27.199

If we separate Dumas' results, and take the mean of the other three, we get in contrast—

Berzelius	27.237
Tissier	27.068
Terreil	27.030
Mean	27.112
Dumas (mean)	27.462

Or, if we throw together only the numbers obtained by Tissier and Terreil, which come nearest to each other, we have—

Tissier	27.068
Terreil	27.030
Mean	27.049
Berzelius	27.237
Dumas (mean)	27.462

Values now generally adopted for Atomic Weight of Aluminum.

The number adopted in some of the more recent chemical handbooks, reports, &c., may be quoted as follows:—

GMELIN: Handbook of Chemistry (Cav. Soc. Trans.)	27.4
WATTS: Dictionary of Chemistry, First Supplement	27.4
W. A. MILLER: Elements of Chemistry, 4th edit.	27.5
MEYMOTT TIDY: Handbook of Modern Chemistry	27.5
FRANKLAND: Lecture Notes for Chemical Students	27.5
THORPE: Quantitative Chemical Analysis	27.26
Agenda du Chimiste (WURTZ' Laboratory, 1879)	27.5
Annuaire du Bureau des Longitudes, 1876	27.4
NAQUET: Principes de Chimie, &c., 3e ed.	27.5
FITTICA: Jahresb. üb. d. Fortsch. d. Chemie, 1878	27.4
ROSCOE u. SCHORLEMMER: Ausf. Lehrbuch d. Chemie (Ger. ed.)	27.3
FRESENIUS: Anleit. z. quant. chem. Analyse, 5te Aufl.	27.5
CLASSEN: Grundr. d. anal. Chemie (quant.)	27.3
KOHLRAUSCH: Leitfaden d. prakt. Physik. 2te Aufl.	27.4
MENDELEJEFF: Paper on the "Periodic Law" (transl.)	27.3
J. P. COOKE, Jr.: The New Chemistry	27.5
J. D. DANA: System of Mineralogy, 5th ed.	27.5
E. S. DANA: Text-Book of Mineralogy	27.3

New Experiments by the Author.

During the last three years I have devoted a large part of m leisure time to a re-determination of this atomic weight, sparing no

pains to attain as precise a result as possible, and aiming especially at the discovery, and as far as possible removal, of sources of error connected with the methods employed. The following general principles have been kept in view :—

1. That each process used should be as simple as possible, and should involve as little as possible of known liability to error.

2. That different and independent processes should be resorted to as the means of checking each other's results, even though it may fairly be assumed that one is more advantageous than another.

3. That each process should be carried out with quantities of material differing considerably from each other in successive experiments.

4. That only such other atomic weights should be involved as may be counted among those already known with the nearest approach to accuracy.

The most scrupulous care was taken in the purification and examination of all the reagents used, and as far as possible vessels of platinum or of hard porcelain were substituted for those of glass.

Means and method of weighing employed.—For the weighings an excellent balance, of Becker's construction, was employed. It was in perfect order, carefully adjusted (especially as regards centre of gravity of beam with average load to be carried), and would bear safely 200 grams in each pan, giving when thus loaded a deflection of the index to the extent of $1\frac{1}{4}$ division of the scale over which it moves for a difference of weight of .0001 gram. All weighings were made by the well-known method of observing the vibrations of the index on either side the position of rest. In one series of experiments *absolute* weights were required, *i. e.*, real equality of weight between the quantities of matter dealt with and the standards of weight with which they were compared ; in these cases the method of "double weighing" was made use of, so as to eliminate any error arising from inequality in length of the arms of the balance. In view of this need, in connection with a part of the research, for absolute weights, directly comparable with those used by Regnault in his determination of the density of hydrogen, I applied to my friend J. E. Hilgard, Esq., in charge of the office of the United States' Coast Survey at Washington, for a comparison of a kilogramme with a weight of the same denomination belonging to the Coast Survey, the value of which latter weight is accurately known in terms of the original "kilogramme of the

Archives" at Paris. He kindly had this comparison made, and sent me the results in detail, showing that my weight was 8.1 milligrammes heavier than the "star kilogramme" which is the standard of reference at Washington (both *in vacuo*), with an uncertainty of comparison not exceeding .1 milligramme, while the "star kilogramme" is certified to as agreeing with the normal "kilogramme of the Archives" within 1.1 milligramme. I had already a 10-gramme weight, professedly normal, but, as it turned out, too light by a very minute fraction of its value, and with these two, checked against each other, a full series of comparisons was made of all the other weights to be employed, the specific gravity of each piece being determined before its final comparison as to weight, so that the real values might all be referred to a vacuum by calculation of the buoyancy in air. Determinations of the specific gravity of all materials and vessels which had to be weighed were also made, and, the barometer and thermometer being observed at the time of each weighing, all weights hereafter mentioned in this paper represent real values *in vacuo*.

Three separate series of experiments were made, by methods to be presently stated. A fourth series was attempted, involving the conversion of metallic aluminum into oxide and determination of the amount of oxygen taken up, but this process was found to be attended with much difficulty from various causes, amongst others from the liability to loss by spirting if the metal were treated with acid in open or small vessels, from the necessity of transfer to such vessels for final ignition if larger ones were at first used, and from the appreciable solubility of the hydrate of aluminum if this were precipitated in order to avoid evaporation of the original solution. The few results obtained in this way agreed generally with those of the other methods, but varied among themselves within unsatisfactorily wide limits, and were manifestly not deserving of equal confidence. Hence the work was not pushed further in this direction.

First Series of Experiments.

Purification of ammonium alum.—Ammonium alum of commerce was dissolved in water, a very little nitric acid added, and the liquid boiled in large glass beakers by passing in a current of steam. When the solution had become cold a little ammonium ferrocyanide was added—a very small quantity sufficed to throw down the traces of iron present—and a little animal charcoal,

previously well boiled with strong hydrochloric and nitric acid and thoroughly washed, was stirred in to aid in the subsidence of the minute amount of very finely divided Prussian blue which had been formed. The clear liquid was after about ten days drawn off, and evaporated until the larger part of the alum crystallized out on cooling. The crystals, of which there was obtained more than a kilogramme, were re-dissolved in hot water, and re-crystallized several times (throwing away all the mother liquors), the last time in a porcelain vessel, and with agitation, so as to obtain a granular crystalline powder, which was washed with cold distilled water.

Re-dissolving in water the so far purified alum, now much reduced in quantity, it became necessary to secure the exclusion of the metals of the fixed alkalies, lest their alums should exist in isomorphous admixture with the pure ammonium alum required. To this end aluminum hydrate was thrown down from the solution by addition of ammonia, using not quite enough of the reagent for complete precipitation. The precipitate was well washed with abundance of water, this tedious process being much expedited by the use of a siphon-filter delivering the liquid drawn off into a large flask connected with a powerful aspirator. The bulk of the precipitate was twice re-dissolved in pure hydrochloric acid (each time avoiding complete solution), thrown down again by ammonia, and again washed.

This hydrate was now dissolved in just the necessary amount of dilute and very carefully purified sulphuric acid, and just the proper amount added of ammonium sulphate prepared from the same sulphuric acid neutralized with ammonia. The quantities were determined by bringing the two solutions to known bulks, ascertaining by experiment on a sample of each how much of the respective salts was present, and measuring off the required volumes to be mixed. After concentrating the mixed solution by evaporation it was allowed to crystallize by cooling, and the crystallization was repeated thrice, each time washing with a little cold water. On the last crystallization pains were taken to regulate the rate of cooling so that as far as possible uniformly small crystalline grains were formed of about a millimetre in diameter, thus avoiding the liability of large crystals to contain cavities, in which mother liquor might be retained, and on the other hand securing the possibility of seeing with a lens, better than could have been done if the alum were in a still finer crystalline powder, that all the

crystals as afterwards used were clear and transparent, and showed no signs of efflorescence.

It should be added that all the aqueous ammonia used as above for the precipitation of aluminum hydrate, and for its reconversion into alum, was recently and carefully prepared from ammonium chloride purified from alcoholic amines by boiling with nitric acid as recommended by Stas,[1] that the last crystallizations were effected from water which had been, in pursuance of the practice of the same chemist, distilled from potassium permanganate and hydrate, and that for these last crystallizations a large platinum dish was used, and care was taken that the solution was not allowed to boil, nor even to remain for any length of time near the boiling point, since I ascertained that ammonium alum, like simple ammonium sulphate, gradually gives off small quantities of ammonia on continued boiling of a strong solution. The very last crystallization was carried out with only a sufficient quantity of the alum for a couple of the final experiments.

The salt thus purified was found to be free from any ascertainable content of foreign substances. It gave no trace of coloration in its solution when tested by a ferro-cyanide, tannic acid, &c., and by sulphuretted hydrogen and ammonium sulphide; and spectroscopic examination showed that the fixed alkaline metals and calcium were absent. Silver nitrate gave no indication of chlorine.

Ignition of ammonium alum.—Difficulties connected with this method.—I proposed to ignite a weighed quantity of this alum, whose distinct crystallization gives it the advantage as to definiteness in the amount of water over the simple sulphate used by Berzelius, and to determine the weight of the aluminum oxide left behind, but careful examination of this process showed that two difficulties were to be feared.

In the first place, having rapidly dried the product of the last crystallization by gentle pressure between folds of smooth filtering paper[2] free from loose fibre, portions were weighed off and exposed to the air at about 22° C., with the hope that before long a constant "air-dried" weight would be obtained. It had been previously ascertained that exposure over sulphuric acid led to large loss of water of crystallization within a short time. It was found, however, that even in the air loss of weight went on for so long a time that

[1] Quoted in Fresenius' Zeitschrift fur analyt. Chemie, 6ter Jahrg., 4tes Heft., S. 423.

[2] This had been previously purified by ample washing with acid and water, and well dried.

it could not possibly be referred to mechanically adherent water only. It is true that this loss fell off very rapidly after the first hour or so, but it was impossible to decide precisely when it began to affect the water of crystallization. In order to fully exhibit this I quote the following results obtained from a single large specimen kept very long on hand in a place carefully guarded against dust.

	Grams.
Original weight of alum after one hour's exposure to the air at 22.5° C.	35.7456
Loss of weight in 1st twenty-four hours	.0088
" " 2nd " "	.0025
" " 3rd " "	.0017
" " 4th " "	.0015
" " 5th " "	.0010
" " 6th " "	.0012
" " 7th " "	0009
" " 8th " "	.0011
" " 9th " "	.0007
" " 10th " "	.0005

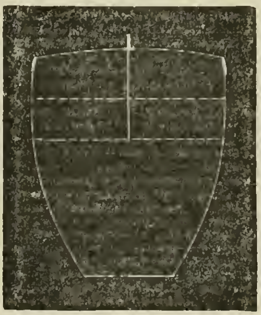
This series of weighings was carried on at longer intervals for six months more; the *monthly* loss was at first .0087 gram, gradually fell off, became as small as .0006 gram in one month of cold weather when the temperature of the room was unusually low, and again rose, with warmer weather, to .0012 gram for the sixth and last month for which the weighings were continued. It was further found that, on placing some of the small crystals of the alum in a glass vessel deep enough to prevent mechanical loss, sensible loss of weight could be produced by the heat developed in simply crushing and pulverizing the salt with a thick square-ended glass rod used as a pestle, and weighed along with the glass and its contents. While, therefore, it might be assumed as probable that mechanically adherent water would be got rid of within a time during which but a very minute quantity of water of crystallization would be lost, a slight doubt is thrown over the exact formula of the salt as analyzed, in reference to this component. Some of the ignition experiments were made with specimens which had been dried by longer exposure to the air than others, as will be noted hereafter.

In the second place it appeared that a minute trace of basic sulphate was retained by the alumina left after ignition at even a very high temperature. This could not be extracted by water, but was detectable by fusion with sodium carbonate free from sulphur,

taking care to use an alcohol flame only. By moistening the alumina with a strong solution of pure ammonium carbonate, re-igniting, and repeating this treatment a second time, it seemed to be possible to remove this source of error, as out of several specimens thus treated only one afforded a barely detectable trace of sulphate.

Details of method adopted.—The actual experiments on the ignition of the alum were carried out as follows. To render uniform the amount of atmospheric condensation on the surface of the vessel weighed, a very light glass bottle was specially made, with a delicately blown stopper, the latter carefully ground in and fitting quite air-tight; the bottle of a size to contain the platinum crucible in which the ignition was to be effected. The crucible was heated to bright redness, and while still quite hot was placed in a desiccator at some distance above a surface of recently distilled sulphuric acid. When cooled down to the temperature of the balance-room the crucible was as quickly as possible transferred to the weighing bottle, which was at once closed, and the combined weight of bottle and crucible was taken. The stopper was then removed for an instant, the cover of the crucible raised, and the quantity of alum desired, which had been roughly weighed off in a tube, having been poured in, occupying in no instance more than one-third

Fig. 1.



depth of the vessel, cover and stopper were replaced, and a second weighing gave, by the gain upon the first, the exact amount of alum used. Attached to the inner side of the crucible cover was a piece of rather stout platinum wire, which, when the cover was in place, ran down into the crucible in the line of its axis of figure,

carrying two little diaphragms of platinum foil perforated with small holes (see fig. 1); such a diaphragm having been suggested and used by Dumas[1] in his researches on atomic weights as the means of preventing any loss of solid particles which might otherwise be carried off mechanically from the substance ignited. To avoid inconvenience from the fusion of the alum in its water of crystallization, and the swelling up of the salt to a bulky, porous mass, the heating was conducted very gradually. The platinum crucible was kept for an hour at 90° C., then for an hour at 100°, for an hour at 110°, another hour at 120°, a like time at 140°, and was then gradually brought to ignition over an argand alcohol lamp. It was then placed inside a larger platinum crucible, resting on a flat bit of unglazed porcelain at the bottom of the latter, and exposed to a gradually increased, and at last bright yellow heat in a gas furnace of Fletcher's construction. This temperature was maintained for a full hour. On cooling down, the smaller crucible was taken out, the cover cautiously raised, and enough of a strong solution of ammonium carbonate introduced to moisten the alumina. Drying gently in a steam-bath, the crucible was reignited over an alcohol blast lamp, producing a strong red heat, and the addition of ammonium carbonate, drying, and ignition once repeated. As soon now as the crucible had ceased to be visibly red hot it was placed in the desiccator as at first, allowed to cool down to the temperature of the balance-room, quickly transferred to the weighing bottle, the stopper of which was inserted, and the final weighing was made while the alumina in the crucible was thus protected from absorption of moisture from the air. These experiments were carried out during a period of remarkably steady weather, with very little variation of atmospheric temperature, pressure, or moisture in the balance-room during the whole series.

Direct results of first series of experiments.—The results were as follows:

A.—Alum dried by exposure to air for 2 hours at 21°–25° C.

I.—8.2144	grams of $(NH_4)_2(Al_2(SO_4)_4.24H_2O$		left	.9258	gram of Al_2O_3.
II.—14.0378	"	"	"	1.5825	"
III.— 5.6201	"	"	"	.6337	"
IV.—11.2227	"	"	"	1.2657	"
V.—10.8435	"	"	"	1.2216	"

[1] Annales de Chimie et de Physique, *loc. cit.*

B.—Alum dried by exposure to air for 24 hours at 19°–26° C.

VI.—12.1023	grams of $(NH_4)_2Al_2(SO_4)_4.24H_2O$		left	1.3660	gram of Al_2O_3.
VII.—10.4544	"	"	"	1.1796	"
VIII.— 6.7962	"	"	"	.7670	"
IX.— 8.5601	"	"	"	.9654	"
X.— 4.8992	"	"	"	.5528	"

(*To be continued.*)

NEW PHENETOL DERIVATIVES.

By Edward J. Hallock.

Para-bromo-ortho-nitro-phenetol is readily prepared from phenetol, by first acting upon it in the cold with pure bromine, and then treating the well washed product with strong nitric acid. The bromo-nitro compound thus obtained is at first a thick oily liquid, which solidifies on standing to a yellow mass of crystals. By recrystallization from alcohol colorless needles were obtained, which melt at 47° C. The compound has an agreeable aromatic odor. This method of preparation is simple, and yields satisfactory results. By reduction with tin and hydrochloric acid it yields, according to Stebbins, a para-bromo-ortho-amido-phenetol.

An attempt was made to prepare the ortho-bromo-para-nitro-phenetol by the action of bromine upon an alcoholic solution of paranitro-phenetol, obtained from phenetol as described in this Journal, **1**, 271. The reaction does not take place smoothly, and the product obtained is not pure When little or no heat is employed, the resultant compound fuses at 54°, a point suspiciously near the melting point of para-nitrophenetol, viz. 58°. The quantity obtained was not sufficient for an analysis. At a higher temperature an entirely different compound was obtained, which melted at about 138° C. The percentage of bromine indicated a mono-bromo-nitro-phenetol. It was contaminated by a small quantity of a yellow dye-stuff slightly soluble in hot water, and possessed of remarkable tinctorial power. The very high melting point of this ortho-bromo-para-nitro-phenetol is somewhat exceptional, and when perfectly pure may be found to differ somewhat

from that above stated. Damm and Staedel[1] state that mono-bromo-para-nitro-anisol melts at 106°.

Ortho-chloro-para-nitro-phenetol is very readily prepared from para-nitro-phenetol by acting on it with potassic chlorate and hydrochloric acid. It forms a yellow oil, solidifying at once to a mass of crystals, which melt, when purified by recrystallization, at 77°. The para-chloro-ortho-nitro-phenetol, as stated in an earlier paper, this Journal, **2**, 258, melts at 61°, a difference of 16° only.

Phenetol is much more easily attacked, it will be seen, by the halogens, chlorine and bromine, than by nitric acid, but in every case the reagent which is first made to act on it forms a para substitution product, while the second substitution takes place in the ortho position; and takes place, generally, with far greater ease than when the para position had not yet been occupied. Does the capture of a para bond weaken that of the ortho carbon atom and render it more defenseless than before?

The following table of melting or boiling points for the phenetol derivatives thus far known will serve to show how the isomeric compounds differ from one another in this respect:

Name of Compound.	Characteristic.	Authority
Para-chloro-phenetol	boils 233°,	Lippmann[2]
Ortho-chloro "	" 208°,	Beilstein[3]
Para-chloro "	" 210°, melts 21°	"
Ortho-nitro "	" 258°,	Groll[4]
Para-nitro "	melts 58°,	Fritzsche[5]
o-Chloro-p-nitro-phenetol	" 77°,	Author
p-Chloro-o-nitro "	" 61°,	Faust[6]
o-Bromo-p-nitro "	" 138°,	Author
p-Bromo-o-nitro "	" 47°,	"

Ortho-bromo-phenetol has not yet been described so far as I can ascertain.

[1]Berl. Ber. **13**, 838; Jahreb. rein. ch. **7**, 311.
[2]Wien. Acad. Ber. **62**, 611.
[3]Berl. Ber. **7**, 1395.
[4]J. pr. Chem. [2], **12**, 207.
[5]Ann. Chem. Pharm. **110**, 155.
[6]Zeitschr. f. Chem. [2], **5**, 1869, 450.

SOUTHERN MEDICAL COLLEGE, ATLANTA, GA., *Jan.*, 1881.

PRELIMINARY NOTICE OF A NEW VEGETABLE COLORING MATTER.

By Sam. P. Sadtler and Wm. L. Rowland.

Some months since our attention was drawn to a variety of wood, called *Beth-a-barra*, which had been recently imported from the west coast of Africa, and was much valued for its extreme toughness and its capability of receiving a high polish.

The wood is compact, very heavy, and in color very nearly resembles ordinary black walnut. On close examination, however, the interstices of the fibres are plainly seen to be filled with a yellow crystalline powder. In this respect it differs from logwood, barwood, camwood and red sandal wood, with which it was compared. In these woods the color is uniformly disseminated, the fibre appearing as if soaked in a solution of corresponding color. It resembles more closely the yellow coloring matter of rhubarb and of araroba, or goa-powder, which compound, chrysophanic acid, occurs also as a loose yellow crystalline powder in the interstices of the root. Special attention was, therefore, paid to its resemblances to this compound, as well as to those of the well-known dye-woods mentioned above.

A cross-section of the Beth-a-barra wood appears very similar to the fernambouc and sappan woods, from which brasilin is obtained.[1] It bears very little resemblance, however, to the sections of logwood and the other therein-mentioned woods.[2]

The coloring principle was extracted from the shavings, or better yet, the sawdust and raspings of the wood, by heating with distilled water containing a little sodium carbonate. This produced a deep claret-red solution, which was then filtered. To the filtrate acetic acid was added in slight excess, precipitating the coloring matter in a fine flocculent condition; this was filtered, washed and then dissolved in hot 80 per cent. alcohol, from which it crystallized upon cooling. By successive crystallizations the pure substance was obtained.

The material thus gotten was a tasteless, yellow compound apparently crystallizing in scales or needles. Upon examination under the microscope these plates are found to be made up of a

[1] Amer. Journ. Pharm. p. 348, 1880. [2] loc. cit. p. 351.

series of flat prisms, joined laterally. The crystals are unchanged in dry or moist air, insoluble in cold water, very slightly soluble in hot water, but readily soluble in alcohol or ether. The presence of even a trace of alkali or alkaline carbonate also causes it to dissolve with deep claret-red color. The crystals melt at 135°C.

Two lots were prepared for analysis; one was dried at 100°C., and the other at 125°C.

Analysis of material dried at 100° C.

	I.	II.	Mean.
Carbon, . .	68.75	68.79	68.77
Hydrogen, . .	6.05	6.05	6.05
Oxygen, . .	25.20	25.16	25.18
	100.00	100.00	100.00

Analysis of material dried at 125° C.

	I.	II.	Mean.
Carbon, . .	75.82	75.00	75.41
Hydrogen, . .	6.39	6.69	6.54
Oxygen, . .	17.79	18.31	18.05
	100.00	100.00	100.00

The mean of the results of the analysis of that dried at 125°C. would give a formula $C_{28}H_{29}O_5$, or possibly $C_{22}H_{23}O_4$, while that dried at 100°C. would be $C_{28}H_{29}O_5+3H_2O$.

The accepted formula for hæmatoxylin, the coloring material of logwood, is $C_{16}H_{14}O_6$[1], which would give 63.57 per cent. of carbon and 4.63 per cent. of hydrogen.

Taking the work done within the past few years on hæmatoxylin as a guide, the action of numerous reagents was then tried upon the new coloring matter. We will give for comparison the results arrived at with hæmatoxylin and then state our results with the Beth-a-barra color.

Sodium amalgam has no action upon hæmatoxylin; with this coloring matter, however, we obtained, on treatment with sodium amalgam, a white compound, which under the microscope is seen to be crystallized in fine needles. The examination of this we reserve for a future communication.

[1]Ber. deutsch. chem. Gesell. 4, 329.

A drop of nitric acid added to the ethereal solution of hæmatoxylin in the cold rapidly oxidizes it; nitric acid oxidizes this coloring principle only when concentrated, and with the aid of heat, giving rise to a white crystalline compound, soluble in ether, which gradually decomposes on exposure to the air.

Hæmatoxylin, when fused with potassium hydrate, yields pyrogallic acid; this material, on fusion with potassium hydrate, yields no pyrogallic acid.

When hæmatoxylin is treated with ammonia solution and is allowed to stand in contact with the air for several days, an oxidation product is obtained[1]; the Beth-a-barra principle, treated in this manner for several days, shows no signs of any oxidation or change.

Reagents.	Brasilin.	Hæmatoxylin.	Santalin.	Beth-a-barra.
Alkalies,	Claret-red sol.	Reddish-purple sol.	Claret-red sol.	Claret-red sol.
Acids—weak,	Orange ppt.	Pink solution,	Light red ppt.	Yellow ppt.
Acids—conc.,	Yellow solution,	" "	Dark red sol.	Yellow sol.
Alum sol.,	Crimson-red ppt.	Yellow solution passing into violet.	Santalin thrown out.	Coloring matter thrown out, does not combine with Al_2O_3
Lime water,	Crimson ppt.	Bluish–purple ppt.	Reddish-brown ppt.	Acts like alkalies.
Ferrous salts,	Purplish-black ppt.	Bluish-black ppt.	Reddish-violet ppt.	Fine reddish chocolate ppt.
Ferric salts,	Brownish-red ppt.	Black ppt.	Reddish-brown ppt.	Chocolate brown ppt.
Copper salts,	Brownish-red ppt.	Purple sol.	Red ppt.	Brown changing to yellow ppt.
Lead salts,	Crimson-red ppt.	Violet sol.	Reddish-violet ppt.	Brick red precipitate.
Mercuric salts,	Yellow ppt.	Yellow sol.	Scarlet ppt.	Orange yellow ppt.
Silver salts,	Yellow ppt.	Gray ppt.	Reddish-brown ppt.	Deep red ppt.
Tartar emetic,	Rose-colored ppt.	Purple sol.	Cherry–colored ppt.	Orange ppt.
Stannous chloride,	Red ppt.	Purple ppt.	Red ppt.	Yellow ppt.
Sodium Aluminate.	Claret-red ppt.	Purple ppt.	" "	Claret-red ppt

It is a noteworthy fact that though this substance contains more hydrogen relatively than brasilin or hæmatoxylin, it does not oxi-

[1] Handwörterbuch d. Chemie, 3, 542.

dize as readily, but is reduced more readily than either of these coloring compounds. The above table has been prepared, comparing the action of a series of reagents upon several of the common coloring principles with the results obtained with this coloring material. The brasilin and santalin were extracted directly from the woods with alcohol, and the other two were alcoholic solutions of the crystallized coloring matters.

The following references, all of them to papers in the Berichte der deutschen chemischen Gesellschaft, show what has been done with the investigation of these vegetable coloring matters in late years: Franz Reim—"Ueber das Hæmatoxylin," 4, p. 329; Adolf Bæyer —"Ueber das Gallein," 4, p. 457; E. Kopp—"Ueber Brasilin und Resorcin," 6, p. 446; C. Liebermann and O. Burg—"Ueber Brasilin," 9, p. 1883; Richard Meyer—"Verhalten des Hæmatoxylins bei der trockenen Destillation," 12, p. 1392; E. A. Letts—"Ueber das Phtaleïn des Hæmatoxylins," 12, p. 1651.

A comparison of the Beth-a-barra coloring material with chrysophanic acid, the yellow coloring principle of rhubarb and goa powder, was then made in order to see what resemblance there might exist between the two.

Chrysophanic acid forms golden-yellow scales, melts at 162°C., forms deep red-colored solutions with caustic alkalies or ammonia, from which the acid is precipitated in yellow flakes on neutralizing the solution with acid. Caustic soda will extract the color from solutions of chrysophanic acid in ether, chloroform, benzol, or petroleum benzin, yielding deep red solutions; ammonia will extract the color from solutions in ether or petroleum benzin, but not from chloroform or benzol solution. An ammoniacal solution is precipitated lilac by acetate of lead and rose-colored by alum.

The Beth-a-barra color looks like chyrsophanic acid, but fuses at 135°C.; forms solutions with alkalies like those of chrysophanic acid. Caustic soda and ammonia both will extract the color from solutions in ether, benzol, petroleum benzin and chloroform. An ammoniacal solution is precipitated brick-red by acetate of lead, and no compound apparently is formed in alum solutions. Chrysophanic acid, when ignited with zinc dust, yields methyl-anthracene; this compound similarly treated yields phenol-like bodies with the odor of wood-tar creosote, and soluble in alkali with violet color. Finally, the percentage composition of this compound, before quoted, differs too decidedly from that of chrysophanic acid, which requires 70.87 per cent. carbon and 3.94 per cent. hydrogen.

Nor does the Beth-a-barra principle correspond exactly with chrysarobin, which Liebermann and Seidler found[1] to be the chief constituent of goa powder. That compound dissolves in strong potassium hydrate solution with yellow color and green fluorescence. Its percentage composition moreover demands 72.29 per cent. of carbon and 5.22 per cent. of hydrogen. By heating with caustic potash solution in contact with air it is changed into chrysophanic acid.

The similarity of the Beth-a-barra principle in many of its reactions to these two compounds leads one to suspect a relationship. We hope to be able to settle what this relationship is shortly by a fuller study of its reactions and derivatives.

PHILADELPHIA, *Dec.* 21, 1880

CONCERNING PHTHALIMIDE.

BY M. KUHARA,

Fellow in Chemistry, Johns Hopkins University

In a paper on the oxidation of orthotoluenesulphamide[2] it has been shown by Remsen and Fahlberg that, when orthosulphobenzoic acid is treated with phosphorus pentachloride and ammonia, it is converted into benzoic sulphinide, $C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right\}NH$. It is probable that the normal chloride of the acid is first formed, and that when this is treated with ammonia, the ammonium salt of sulphaminebenzoic acid is formed, which when treated with hydrochloric acid yields the sulphinide:

$$C_6H_4\left\{\begin{matrix}SO_2Cl\\COCl\end{matrix}\right.+4NH_3+H_2O=C_6H_4\left\{\begin{matrix}SO_2NH_2\\COONH_4\end{matrix}\right.+2NH_4Cl, \quad \text{and}$$

$$C_6H_4\left\{\begin{matrix}SO_2NH_2\\COONH_4\end{matrix}\right.+HCl=C_6H_4\left\{\begin{matrix}SO_2\\CO\end{matrix}\right\}NH+H_2O+NH_4Cl.$$

It seemed probable from a consideration of these reactions that phthalic acid when treated in a similar way would yield phthalimide, and, at the suggestion of Professor Remsen, I have made some experiments in the direction indicated.

[1] Ber. d. deutsch. chem. Ges. **11**, 1603.   [2] This Journal. **1**, 426.

Phthalyl chloride was made according to the directions of Ador,[1] by boiling phthalic acid (1 mol.) with phosphorus pentachloride (2 mol.) and a little oxychloride. On treating this with aqueous ammonia it passed into solution, and now on adding hydrochloric acid a bulky precipitate was produced. This dissolved easily by heating; on cooling, a mixture of white scaly crystals with a minute quantity of fine needles was deposited, while on still further concentrating the mother liquor phthalic acid crystallized out. By recrystallizing the mixture from alcohol, beautiful transparent rhombohedral crystals were obtained, and from the mother-liquors the needle-shaped crystals mentioned above were deposited. The rhombohedral crystals, which were obtained in larger quantity than the needles, were analyzed:

I. 0.2 gram gave 14.74 cc. N after corrections.

II. 0.196 gram gave 14.78 cc. N after corrections.

A substance of the formula $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH$, that is of the formula of phthalimide, requires 9.52 per cent. N, while the quantities found correspond to 9.21 and 9.42 per cent. respectively.

The substance is, however, quite distinct from phthalimide. It is soluble in cold alcohol and water, more readily in boiling alcohol and water, while phthalimide is not soluble in cold alcohol and water. It melts without decomposition when heated, and sublimes in flakes. It dissolves in concentrated sulphuric acid and water, throwing down phthalic anhydride from the solution. It melts at 192°, the imide at 230°. It gives no precipitate with silver nitrate.

From the knowledge thus far gained it seems as though this substance must be regarded as an isomeride of phthalimide. According to von Gerichten[2] it appears probable that phthalyl chloride is either $C_6H_4\left\{\begin{matrix}CCl_2\\CO\end{matrix}\right\}O$, or a mixture of this substance with the normal chloride. If this view is correct, the formation of a substance isomeric with phthalimide might easily be accounted for. The action of ammonia upon a substance of the formula $C_6H_4\left\{\begin{matrix}CCl_2\\CO\end{matrix}\right\}O$ might give rise to a product of the formula $C_6H_4\left\{\begin{matrix}C(NH)\\CO\end{matrix}\right\}O$, which would be isomeric with phthalimide. The formation of such a substance would be exceedingly interesting and its study attractive. I regret to say that though I made re-

[1]Annalen der Chemie, **164**, 230. [2]Berichte d. deutsch. chem. Gesell. **13**, 417

peated efforts to get possession of more of this product, they all failed, and I was obliged to give up its study. It is strange that in the first experiment just exactly the right conditions for its formation should have been found, and that these could not again be met with.

In the subsequent experiments it was found that when phthalyl chloride is treated with ammonia and hydrochloric acid, phthalic anhydride is precipitated. It was also shown that when ammonium phthalamate is treated with hydrochloric acid, phthalic anhydride is precipitated. When phthalyl chloride is dissolved in ammonia and the solution concentrated to a very small volume, phthalamic acid, $C_6H_4\left\{\begin{matrix}COOH\\CONH_2\end{matrix}\right.$, is deposited. This was carefully compared with phthalamic acid prepared from phthalic anhydride, according to Marignac's directions,[1] and the two were found to be identical.

The connection known to exist between phthalic anhydride, phthalamic acid, phthalimide and phthalyl chloride, would then lead to the conclusion that all these bodies have a similar structure. Phthalamic acid is made from ammonium phthalate by heating, and the only equation which will represent this reaction satisfactorily is the one commonly used:

$$C_6H_4\left\{\begin{matrix}COONH_4\\COONH_4\end{matrix}\right.-NH_3-H_2O=C_6H_4\left\{\begin{matrix}CONH_2\\COOH.\end{matrix}\right.$$

Further, when phthalamic acid is heated it gives off water and is converted into phthalimide:

$$C_6H_4\left\{\begin{matrix}CONH_2\\COOH\end{matrix}\right.-H_2O=C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH.$$

It is possible, of course, to conceive of the formation of the isomeric substance, $C_6H_4\left\{\begin{matrix}C(NH)\\CO\end{matrix}\right\}O$, under these circumstances, but its formation does not appear probable. While then it is impossible to decide positively what the formula of phthalimide is, the probabilities are in favor of the one commonly accepted.

Now, when phthalyl chloride is treated with gaseous ammonia it is converted directly into phthalimide. The reaction takes place very easily, and is accompanied by a decided evolution of heat. The substance possessed all the properties of phthalimide as described by Laurent and Marignac. The yield was excellent;

[1] Annalen der Chemie, **42**, 219.

apparently almost quantitative. Assuming that phthalimide has the commonly accepted formula, the only way to represent this transformation of the chloride satisfactorily is by the equation:

$$C_6H_4\left\{\begin{matrix}COCl\\COCl\end{matrix}\right.+3NH_3=C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH+2NH_4Cl.$$

But this leads to the view that the chloride has the normal structure, whereas, as was stated above, the experiments of von Gerichten indicate that the chloride is $C_6H_4\left\{\begin{matrix}CCl_2\\CO\end{matrix}\right\}O$. It is possible that a substance isomeric with phthalimide is formed when phthalyl chloride is treated with ammonia, and that this is then converted spontaneously into the imide.

A few derivatives of phthalamic acid were made, as this substance has been but very imperfectly studied. The only salts of the acid which have hitherto been prepared are those of silver and ammonium. In order to prepare the imide it was found most convenient to pass dry ammonia into a flask containing phthalic anhydride, slightly heated. A violent reaction took place, the mass instantly melting, and then soon solidifying again. The solid mass was essentially pure imide.

To an aqueous solution of phthalimide there was added an excess of baryta water and the two boiled together. A current of carbon dioxide was then passed through the cooled solution, the precipitated barium carbonate filtered off, and the clear filtrate concentrated. The salt does not crystallize from an aqueous solution, the latter finally becoming syrupy in consistency and remaining so even after long standing. If alcohol be added to the concentrated aqueous solution the salt is thrown down as a white, amorphous powder, being entirely insoluble in alcohol. This was filtered off, dried and analyzed:

0.1135 gram precipitated barium salt gave 0.057 gram $BaSO_4$.

Calculated for $\left(C_6H_4\left\{\begin{matrix}CONH_2\\CO_2\end{matrix}\right.\right)_2Ba$	. .	29.46 per cent. Ba.
Found	. .	29.47 " "

Potassium phthalamate, $C_6H_4\left\{\begin{matrix}CONH_2\\COOK.\end{matrix}\right.$ This salt was prepared by the gradual addition of a very dilute solution of potassium sulphate to the solution of the barium sulphate. After

filtering off the precipitated barium sulphate, the solution was left to evaporate slowly over sulphuric acid. After several days, very fine, silky, transparent needles crystallized out. It is easily soluble in alcohol and water. It gives off ammonia when boiled with potassium hydroxide, and hydrochloric acid throws down phthalic anhydride from its solution.

Copper phthalamate was prepared from the barium salt by precipitating with a solution of copper sulphate. It does not crystallize, but gradually separates in the form of an amorphous powder.

Phthalamic is an exceedingly weak acid and its salts are not well characterized compounds.[1]

Contributions from the Chemical Laboratory of Harvard College.

IX.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

SUBSTITUTED BENZALDEHYDES.[2]

By J. Fleming White.

The ortho- and parachlorbenzaldehydes are the only compounds of this class containing a single halogen atom which have been described heretofore. The former, made by Henry[3] from salicylal-

[1]The fusing point of phthalic acid has been the subject of considerable discussion, the last statement bearing upon it having come from E. Ador (Annalen der Chemie, **164**, 239). Ador says that crystallized phthalic acid melts at 213° and the powder of the same substance at 203°. The discrepancies in the statements on record seem to be due to the fact that when the acid is heated, it is partly converted into its anhydride before its fusing point is reached. The presence of the anhydride tends to lower the fusing point, and this is the lower the more anhydride there is formed. If the acid is heated slowly, or if it be used in the form of powder, more anhydride is formed and the fusing point is lower. Some special experiments were made with the pure acid to test the correctness of this view. Small quantities were heated in U-tubes placed in paraffin baths at the temperatures of 140° and 170°. In both cases anhydride was formed and the fusing point of the acid considerably lowered. Under exceptional conditions the fusing point of pure phthalic acid may be observed as high as 213°, but usually it will be found to vary considerably. To test the purity of the acid, it is advisable to make the anhydride and then crystallize this, when pure, from water.—I. R.

[2]Presented to the American Academy. Communicated by the Authors.

[3]Ber. d. ch. G. **2**, 135.

dehyde by treating it with an excess of phosphoric pentachloride and decomposing the orthochlorbenzalchloride ($C_6H_4ClCHCl_2$) formed with water in a sealed tube at 170°, was a heavy colorless oil boiling between 210° and 220° and oxidized even by the air into orthochlorbenzoic acid.

The so-called parachlorbenzaldehyde was first made by Beilstein and Kuhlberg[1] by boiling chlorbenzylchloride, $C_6H_4ClCH_2Cl$, with plumbic nitrate and water, according to the method of Lauth and Grimaux[2]; also by heating chlorbenzalchloride, $C_6H_4ClCHCl_2$, with water in a sealed tube at 170°, and by treating benzaldehyde with chlorine in presence of iodine. Later, Berlin[3] obtained it by distilling trichlorbenzylamine, $(C_6H_4ClCH_2)_3N$, with bromine and water, and Sintenis by the action of chlorine on chlorbenzylethylether, $C_6H_4ClCH_2OC_2H_5$. They all describe it as a heavy oil, and Berlin gives its boiling-point as 210°–220°.

As the chlorine compounds used by Beilstein and Kuhlberg, Berlin and Sintenis[4] were all made by the action of chlorine on toluol in the cold, and must therefore have contained the corresponding ortho-compounds,[5] a revision of their work is necessary.

Parachlorbenzaldehyde, C_6H_4ClCOH, was made by boiling 10 grams of parachlorbenzylbromide, melting-point 48°, with 14 grams of plumbic nitrate and 100 grams of water for three days in a flask with a return-cooler, which was kept full of carbonic dioxide during the boiling and subsequent distillations to prevent oxidation of the aldehyde by the air. The aldehyde, separated by distillation from the plumbic ~~bromide~~ chloride formed, solidified in the cooler in long white needles, which were purified by solution in acid sodic sulphite and filtering; the filtrate concentrated by evaporation deposited on cooling crystals of the double salt of the aldehyde and acid sulphite, which were washed twice with cold alcohol, dried, dissolved in a small quantity of hot water, and decomposed by distillation with solid sodic carbonate. The pure aldehyde, thus obtained, was dried over sulphuric acid in an atmosphere of carbonic dioxide and analyzed.

0.2112 gram gave on combustion 0.4613 gram CO_2 and 0.0680 gram H_2O.

	Calculated for C_7H_5ClO.	Found.
Carbon	59.78	59.56
Hydrogen	3.56	3.57

[1]Ann. Chem. Pharm. **147**, 352. [2]Ibid. **143**, 80. [3]Ibid. **151**, 140. [4]Ber. d. ch. G. **4**, 697. [5]This Journal, **2**, 85.

Properties. Long white needles melting at 47°, which sublime very easily; slightly soluble in water, very soluble in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. Potassic permanganate oxidizes it rapidly, air slowly, converting it into parachlorbenzoic acid.

The following substituted aldehydes were prepared from the corresponding bromides by the same method. In solubility they all resemble the parachlorbenzaldehyde.

Parabrombenzaldehyde, C_6H_4BrCOH.

0.5000 gram of the substance gave on combustion 0.8268 gram CO_2 and 0.1298 gram H_2O.

	Calculated for C_7H_5BrO.	Found.
Carbon	45.40	45.10
Hydrogen	2.70	2.88

Long white needles melting at 57°. With oxidizing agents or air it forms parabrombenzoic acid.

Paraiodbenzaldehyde, C_6H_4ICOH.

0.7339 gram of substance gave on combustion 0.9665 gram CO_2. The hydrogen was unfortunately lost.

	Calculated for C_7H_5IO.	Found.
Carbon	36.20	35.90

White needles melting at 73°. With oxidizing agents it forms paraiodbenzoic acid.

Metabrombenzaldehyde, C_6H_4BrCOH.

0.5900 gram of substance gave on combustion 0.9800 gram CO_2 and 0.1320 gram H_2O.

	Calculated for C_7H_5BrO.	Found.
Carbon	45.40	45.30
Hydrogen	2.70	2.49

A colorless heavy oil, showing no signs of solidifying even in a freezing mixture of ice and salt. With oxidizing agents, or on exposure to the air, gives very easily metabrombenzoic acid.

Orthobrombenzaldehyde, C_6H_4BrCOH, was prepared from the liquid orthobrombenzylbromide, as this work was done before it

had been obtained in the solid state. Instead of distilling the product of the reaction, the plumbic bromide and water were decanted while hot, leaving the aldehyde as a heavy oil, which was washed with water, purified as before described with acid sodic sulphite, dried, and analyzed.

0.5440 gram of substance gave, on combustion, 0.8990 gram CO_2 and 0.1476 gram H_2O.

	Calculated for C_7H_5BrO.	Found.
Carbon	45.40	45.08
Hydrogen	2.70	3.01

A heavy colorless oil, much more rapidly oxidized by the air than any of the other substances described in this paper.

The three para-compounds yielded, when treated in alcoholic solution with sulphuretted hydrogen, the thioaldehyde, as a reddish white varnish, which it did not seem worth while to investigate.

X.—ON FURFUROL AND CERTAIN OF ITS DERIVATIVES.[1]

By Henry B. Hill.

In December, 1876, by the kind invitation of Dr. E. R. Squibb, I had the opportunity to examine the working of a new process for the manufacture of acetic acid by the dry distillation of wood at a low and carefully regulated temperature, as it was carried on under his direction at Brooklyn, N. Y. I then noticed that, in the rectification of the crude wood spirit, a yellowish oil passed over with the vapor of water after the more volatile portions had been distilled off. Its high specific gravity and its peculiar odor made me anxious to examine it more closely.

A short study of it was sufficient to show that it contained large quantities of furfurol, which could be isolated in a pure state with little trouble, and I therefore undertook at once the study of the constitution of furfurol and pyromucic acid. Before my investigations were far advanced, Baeyer[2] published the first of his papers upon the constitution of furfurol, in consequence of which my own

[1] Proceedings Amer. Acad. of Arts and Sciences. Communicated by the Author.

[2] Berichte der deutsch. chem. Gesellsch. **10**, 355.

work was naturally discontinued. At the same time, however, I wrote to Professor Baeyer asking if I could not make use of the large supply of material which I had at hand without interfering with the plan of his research. In reply I received the extremely considerate intimation that a study of mucobromic acid and its derivatives would in no way interfere with his work.

This investigation was begun in 1877; and, although it is not yet completed, so many facts have accumulated that I have thought it best to publish an account of the results already obtained.

Different portions of this research I have carried on with Mr. O. R. Jackson and Mr. C. F. Mabery, assistants in this laboratory, and with Mr. W. Z. Bennett. In my description of our results I shall make plain the share which each of these gentlemen has had in the work.

My most sincere thanks are due to Dr. Squibb for the generous supply of material, without which it would have been impossible for me to have undertaken this investigation.

Furfurol one of the Products of the Dry Distillation of Wood.

Although the products formed in the dry distillation of wood have repeatedly been made the subject of investigation, I can find in the literature of the subject but little reference to the presence of furfurol among them. That furfurol is thus formed is asserted by Gmelin[1] on the authority of Völkel, but a close examination of Völkel's original papers[2] fails to show any sufficient foundation for the assertion. Although Völkel had already shown that furfurol was formed in the dry distillation of sugar, and had established its presence by analysis[3], in his subsequent work upon the dry distillation of wood he seems to have based his conclusions solely upon qualitative tests by no means conclusive. Although he makes a number of general statements concerning the presence of furfurol among the products he obtained, I can find nothing more definite than is contained in the following passage[4]:

After describing the extraction of a yellowish brown oil from the pyroligneous acid by means of ether, he proceeds: "In Kalilauge löst sich das Oel unter Entwicklung eines betäubenden Geruchs auf, der von einer geringen Menge einer organischen Basis herrührt,

[1]Gmelin's Handbuch, **7**, 599; Suppl. **2**, 972.
[2]Poggendorff's Annalen, **82**, 496; **83**, 272 and 557; Ann. Chem. u. Pharm. **86**, 66.
[3]Ann. Chem. u. Pharm. **85**, 59.
[4]Ibid. **86**, 83.

weil er auf Zusatz von Säure wieder verschwindet. Die dunkel gefärbte alkalische Lösung trübt sich in kurzer Zeit durch Ausscheiden eines gelbbraunen Körpers, der Pyroxanthin enthält. Aus der abfiltrirten noch stark gefärbten alkalischen Flüssigkeit wird durch verdünnte Schwefelsäure ein anderer brauner Körper abgeschieden, und zugleich der Geruch des Kreosots wahrgenommen. Aus diesen Reactionen ergiebt sich dass das Oel . . . ein sehr gemengtes . . . ist. Es enthält ein eigenthümliches Oel (Pyroxanthogen), das durch die Einwirkung von Alkalien in Pyroxanthin übergeht; Kreosot; ferner mehrere flüchtige Oele, die durch Alkalien in braune Körper umgeändert werden die in Kali theils löslich theils unlöslich sind. Diese letzteren Oele sind unstreitig identisch mit den flüchtigeren Oelen die bei der Destillation des Zuckers erhalten werden, Furfurol, u. s. w." I have quoted the passage with but little abbreviation, that the character of the qualitative tests upon which Völkel based his conclusion may be appreciated.

Quite recently since the publication of a preliminary note by me upon this subject, V. Meyer[1] has found in the commercial glacial acetic acid of the continent, a small quantity of furfurol which manifested itself by the intense red color developed when the acid was mixed with aniline.

Although these two observations are all I can find recorded of the presence of furfurol among the products of the dry distillation of wood, its formation from wood by other means has been more frequently noticed. Although Döberciner[2] could obtain no furfurol from sawdust by distillation with sulphuric acid, Fownes[3] none from linen, and Cahours[4] and Gudkow[5] were equally unsuccessful with pure cellulose, Emmet[6] obtained it by the same method from woody fibre, Stenhouse[7] from sawdust, afterward from mahogany[8] and madder.[9] Gr. Williams[10] also found that it was formed when wood was heated under pressure with water, although none could be obtained at ordinary pressures. Similar results were obtained by H. Müller.[11]

A brief description of the method of distillation which has furnished the material for this investigation may prove of interest:

[1]Berichte der deutsch. chem. Gesellsch. **11**, 1870.
[2]Journ. prakt. Chem. **46**, 168.
[3]Pharmaceutical Journal and Transactions, **8**, 113.
[4]Ann. Chim. Phys. [3] **24**, 277.
[5]Zeitschr. für Chem. 1870, 360.
[6]Am. Jour. **32**, 140.
[7]Ann. Chem. u. Pharm. **35**, 301.
[8]Ibid. **74**, 278.
[9]Ibid. **80**, 325.
[10]Chem. News, **26**, 231 and 293.
[11]Ibid. **26**, 247.

since the product obtained in this way contains considerable quantities of furfurol, while the percentage formed by the ordinary methods must be very small to have escaped notice so generally. The wood, chiefly oak, is cut into small pieces and filled into rectangular retorts of boiler iron, each one capable of holding a charge of from five to six thousand kilogrammes. The retorts when charged are placed in separate cells of an oven heated by hot-air flues. The temperature of this oven is carefully regulated by means of long mercurial thermometers built into each cell, and the thermometer readings vary from 150° at the beginning of a distillation to 200° at the end. The average time required is six days, and during this time the wood loses about thirty-two per cent. of its weight. The volatile products pass through an outlet pipe at the top of each retort, and are condensed in a set of ordinary coolers.

The wood left in the retorts after distillation is darker in color and somewhat more brittle than the fresh wood: its composition agrees essentially with that given by Payen[1] for dried oak wood. The specimens of wood for analysis were taken while still warm from the retorts, and kept hermetically sealed until analyzed.

I. 0.4480 gram substance gave 0.8950 gram CO_2, 0.2545 gram H_2O and 0.0040 gram ash.

II. 0.3880 gram substance gave 0.7810 gram CO_2 and 0.2220 gram H_2O. 1.2725 gram of the same wood gave 0.0070 gram ash.

III. 0.3270 gram substance gave 0.6390 gram CO_2, 0.1740 gram H_2O and 0.0015 gram ash.

	Found.			Payen.
	I.	II.	III.	
C	50.01	54.89	53.30	54.44
H	5.88	6.29	5.78	6.24
Ash	0.89	0.55	0.46	

The volatile products of the distillation are subjected to the ordinary processes of rectification. In fractioning the wood spirit, after the more volatile portions have passed over, the distillate throws down a heavy yellow oil upon dilution with water, and somewhat later the slightly acid aqueous distillate contains an abundance of the same heavy oil in suspension. The quantity of oil which thus separates in the course of distillation amounts to between three and four tenths of one per cent. of the crude wood spirit taken, although I am unable to form even an approximate estimate of what proportion this may be of the total amount present.

[1] N. Ann. Sci. Nat. **11**, 24.

The oil, as I received it, was feebly acid to test paper, and had a peculiar aromatic odor. It was bright yellow in color, and slightly heavier than water. It was washed with water, dried over calcic chloride and submitted to fractional distillation. The liquid began to boil a little above 100°, but the thermometer rose rapidly and had reached 160° before any considerable quantity had passed over; between 160–170° it remained stationary for a long time, and then rose again rapidly to over 200°. After several distillations, about sixty per cent. of the oil taken distilled between 160° and 165°, the greater part of which boiled steadily at 162°. The boiling point and general character of the oil at once suggested the presence of furfurol, and this was readily proved by its conversion into furfuramide, furfurine, and pyromucic acid. The behavior of the oil to alkalies, however, showed that it was still by no means homogeneous. When shaken with a dilute solution of potassic or sodic hydrate, a brilliant yellow color was developed; and in a few moments the clear liquid became turbid with the separation of a flocculent yellow precipitate, which proved to be chiefly pyroxanthin. In following out the method of purification which was thus suggested I found it most convenient to separate from the crude oil only so much of the higher boiling constituents as could be removed by rejecting that which passed over above 175° in two successive distillations. The distillate collected below 175° was then gradually mixed with one-fourth its volume of a concentrated solution of sodic hydrate, taking care to keep the mixture cool, and shaking the two well together. After standing a short time the oil was separated from the alkaline solution, washed with a little water, and distilled with steam. The furfurol thus obtained was sufficiently pure for all ordinary purposes, and from such a product was made all the pyromucic acid which has been used in the course of the following investigations.

For its conversion into pyromucic acid it was mixed with an equal volume of a concentrated alcoholic solution of sodic hydrate, and carefully stirred until the violent reaction was over. The sodium salt was then thoroughly washed with ether, dissolved in hot water, and decomposed by concentrated hydrochloric acid. For the purification of the crude acid it was dissolved in a cold dilute solution of sodic carbonate, taking care that the solution should remain slightly acid. The filtered solution of the sodium salt was boiled with bone-black, filtered, concentrated by evaporation, and

finally acidified with hydrochloric acid. The acid which separated on cooling was then recrystallized from boiling water, and was found on analysis to be sufficiently pure for further use.

0.8140 gram substance gave 1.5910 gram CO_2 and 0.2910 gram H_2O.

	Calculated for $C_5H_4O_3$.	Found.
C	53.57	53.31
H	3.57	3.97

The acid prepared in this way melted at 128–129°; and, since the melting point of pyromucic acid is usually given somewhat higher, it seemed advisable to subject this product to further purification. Mr. J. J. Thomsen, therefore, prepared the ethyl-ether of the acid by saturating its solution in absolute alcohol with hydrochloric acid, precipitating with water, and washing first with a dilute solution of sodic carbonate and then with water. He then found that the carefully dried ether distilled from the first drop to the last unchanged at 195° (mercury column completely in vapor) under a pressure of 766 mm. On cooling, it crystallized in large transparent prisms, which melted at 34°. According to Malaguti[1], ethyl pyromucate melts at 34°, but boils at 208–210°, under a pressure of 756 mm. For the determination of boiling point we employed about 30 grams of the ether, and an analysis showed its purity.

0.5615 gram of substance gave 1.2330 gram CO_2 and 0.2940 gram H_2O.

	Calculated for $C_5H_3O_3C_2H_5$.	Found.
C	60.00	59.87
H	5.71	5.81

A portion of this ether was saponified with sodic hydrate, the acid liberated from the sodic salt, recrystallized from hot water several times, and finally melted. The solidified acid melted at 130.5° (uncor.), while an acid made directly from mucic acid melted at 130°. The corrected melting points of the two were 133° and 132.5°; whereas Schwanert[2] gives the corrected melting points 134.3° and 132.6° respectively for substance made from furfurol and from mucic acid. The chief constituent of the oil under investigation was thus shown to be furfurol. From the higher boiling portions I have as yet been able to isolate no well-marked substances. On distillation, the thermometer rose slowly to over 300°, and even after long fractioning there appeared to be no tendency towards

[1] Ann. Chim. Phys. [2] **64**, 279. [2] Ann. Chem. u. Pharm. **116**, 257.

constant boiling points. By far the greater portion was insoluble in alkalies, and I could obtain no characteristic derivatives by the action of various reagents.

From the sodic hydrate used for washing the crude furfurol could be separated in small quantity an oil volatile with steam, and possessing a strong odor like smoked fish. It had the general characters of a phenol, but I have not as yet further identified it. Since a large quantity of material has been accumulated in preparing the furfurol necessary for the following researches, I hope before long to make further study of the less volatile constituents which are present in smaller quantity.

Mucobromic Acid.

Mucobromic acid was first made by Schmelz and Beilstein[1], in 1865, by the action of bromine and water upon pyromucic acid. They found its salts so unstable that they made little attempt to isolate them, but confined themselves chiefly to the study of the decomposition which ensued when it was boiled with alkalies, and of the reaction effected by argentic oxide.

They found that the acid was rapidly decomposed when boiled with baric hydrate, that bromacetylen was set free, and that baric carbonate was precipitated. In solution, they found, beside baric bromide, a sparingly soluble barium salt, to which they gave the name baric muconate, and the formula $BaC_4O_3.H_2O$. This formula was, however, based upon a single barium and two water determinations. They also prepared the free muconic acid, but made no further study of it than to establish the fact that it was a crystalline solid readily soluble in water, and that its lead salt was insoluble. They expressed the reaction which they supposed had taken place by the equation:

$$2C_4H_2Br_2O_3+H_2O=C_4H_2O_3+C_2HBr+2CO_2+3HBr.$$

They also found that mucobromic acid was attacked when boiled with argentic oxide and water, that argentic bromide was formed, and at the same time a silver salt quite insoluble in water. This silver salt, according to their calculations of the analytical results which they obtained, had the formula $C_7H_2Br_3Ag_3O_5$, and they regarded this as an intermediate product standing between mucobromic and muconic acids. The acid was found to be a crystalline

[1]Ann. Chem. u. Pharm. Suppl. 3, 276.

solid, which appeared to give bromacetylen and muconic acid when heated with baric hydrate. The reaction with argentic oxide they wrote:

$$2C_4H_2Br_2O_3 + 2Ag_2O = C_7H_2Br_3Ag_3O_5 + AgBr + H_2O + CO_2.$$

In the course of the investigations upon mucic acid and its derivatives, which were begun in Limpricht's[1] laboratory in 1868, mucobromic acid received more or less attention. Although it was found to be the only product when pyromucic acid was treated with water and an excess of bromine at ordinary pressures, Limpricht and Delbrück showed that it was completely decomposed when heated in a sealed tube to 120° with bromine and water, provided that three molecules of bromine, at least, were used to one of mucobromic acid. As products of the decomposition, they found, beside carbonic dioxide and hydrobromic acid, tribromethylenbromide, C_2HBr_5, perbromathylenbromide, C_2Br_6, tetrabrombutyric (?) acid, $C_4H_4Br_4O_2$, and dibromfumaric (?) acid, $C_4H_2Br_2O_4$. The marks of interrogation appear in Limpricht's original paper. Limpricht and Lessing also found in one experiment that, by the reduction of mucobromic acid, a liquid was formed which boiled at about 120° and contained 84.8 per cent. of carbon, 8.8 of hydrogen, and the remaining 6.4 per cent. was oxygen. They were, however, unable to repeat the experiment with a like result.

In attempting the preparation of mucobromic acid, Mr. O. R. Jackson and I found that we were unable to obtain a satisfactory yield by following the method given by Schmelz and Beilstein or by Limpricht. Schmelz and Beilstein say that the quantity of water taken is not a matter of indifference, but neither they nor Limpricht make any specific statements as to the amount which they found to be most advantageous. They agree, however, that the bromine should be added slowly as long as it is taken up in the cold, that the solution should then be heated and bromine added as long as the color continues to disappear.

According to this method we were unable to get more than 25 per cent. of the theoretical yield; and at the same time we were obliged to use quite a large excess over the amount of bromine calculated from the equation:

$$C_5H_4O_3 + 4Br_2 + 2H_2O = C_4H_2Br_2O_3 + CO_2 + 6HBr.$$

[1] Berichte d. deutsch. chem. Gesellsch. **2**, 211; **3**, 90, 671; **4**, 805; Zeitschr. für Chem. 1869, 599; Ann. Chem. u. Pharm. **165**, 253.

We soon found that our yield was greatly increased and the excess of bromine proportionately decreased if the bromine was added rapidly. Later, when it was found that a low temperature was essential to the formation of mucochloric acid, the pyromucic acid and water were cooled with ice until the bromine had all been added, but the yield was not perceptibly affected.

We have obtained the best results by the following method: Pyromucic acid is suspended in ten times its weight of water contained in a flask fitted with reverse cooler and drop-funnel. The calculated amount of bromine is then rapidly added, cooling only so far as may be necessary to avoid loss of bromine. After the bromine is all added, the flask is heated, and the liquid kept boiling for ten or fifteen minutes. The solution may then be allowed to crystallize direct, although we have usually evaporated it until the hydrobromic acid began to volatilize in abundance before allowing it to cool. In either case the crystals should be well washed with cold water and recrystallized from boiling water. In this way we have found it easy to obtain 70 per cent. and over of the theoretical yield.[1]

The acid recovered from the mother liquors is usually very dark colored, and it cannot be purified by recrystallization from water either with or without the addition of bone-black. We have found, however, that such an acid may be obtained perfectly white by one or two recrystallizations from dilute sulphuric acid (1 : 4).

As to the properties of mucobromic acid, we can only confirm the statements of Schmelz and Beilstein. It crystallizes ordinarily from water in irregular leafy aggregates, from acid solutions or from certain other solvents in distinct rhombic plates. From a solution in concentrated hydrobromic acid we have frequently obtained it in large compact crystals, with edges 10 to 12 mm. in length, but so striated as to render measurement impossible. It is sparingly soluble in cold water, very readily in hot water, in alcohol or in ether. In benzol or carbonic disulphide it is very sparingly soluble in the cold, but dissolves quite readily on heating. Chloroform takes up a little when hot, most of which it deposits on cooling. In warm concentrated sulphuric acid it dissolves freely, and, if not too strongly heated, crystallizes out on cooling or on dilution. It melts at 120–121°, and at a higher temperature it distils in part unchanged.

[1]Under conditions favorable to complete crystallization from the concentrated hydrobromic acid which forms the mother liquors, we have obtained 78 per cent.

The following analyses may serve to show the purity of the material used in the course of the following investigations:—

I. 0.7840 gram substance gave 0.5390 gram CO_2 and 0.0720 gram H_2O.

II. 0.9326 gram substance gave 0.6340 gram CO_2 and 0.0712 gram H_2O.

III. 0.2347 gram substance gave 0.3421 gram AgBr.[1]

IV. 0.2331 gram substance gave 0.3410 gram AgBr.

	Calculated for $C_4H_2Br_2O_3$.	Found. I.	II.	III.	IV.
C	18.60	18.75	18.55		
H	0.77	1.02	0.85		
Br	62.02			62.03	62.25

Salts of Mucobromic Acid.

Schmelz and Beilstein found that mucobromic acid decomposed baric carbonate, and that the barium salt thus formed was readily soluble in water, although it was decomposed during the spontaneous evaporation of the solution. As it seemed a matter of some interest to determine whether mucobromic acid was capable of forming salts, Mr. O. R. Jackson and I pursued the investigation one step further.

Baric Mucobromate, $Ba(C_4HBr_2O_3)_2$. We found that an aqueous solution of mucobromic acid dissolved baric carbonate readily, that the solution on standing soon turned brown, deposited a brownish flocculent precipitate, and contained then a baric bromide in abundance. On heating, the same change took place more rapidly, and when the solution was boiled a substance was volatilized with the steam which had a sharp, acrolein-like odor, and reduced silver oxide on heating. Although this change was rapid near 100°, we found that it was sufficiently slow at 50-60° to allow the preparation of a solution saturated at this temperature, which on cooling with vigorous stirring deposited crystals of the barium salt. The mucobromic acid was suspended in very little water, the whole warmed to 50-60°, baric carbonate added in excess, and the solution filtered and cooled as rapidly as possible. Even with these precautions we found it difficult to saturate the acid completely without bringing about decided decomposition. The salt, therefore,

[1] All the determinations of halogens in this and the subsequent investigations were made according to the method of Carius.

usually contained more or less free acid, from which it could be completely freed by washing with ether. The salt when dried *in vacuo* over sulphuric acid hardly lost weight at 100°, but when heated a few degrees higher it turned brown and gave out the sharp, penetrating odor mentioned above. Analyses I. and II. were made with a preparation crystallized from water without subsequent washing, III., IV., and V. with substance washed with ether.

I. 0.9479 gram gave 0.5018 gram CO_2 and 0.0547 gram H_2O.

II. 0.3434 gram gave, on ignition with H_2SO_4, 0.1165 gram $BaSO_4$.

III. 0.4186 gram gave, on ignition, 0.1482 gram $BaSO_4$.

IV. 0.5747 gram gave, on ignition, 0.2030 gram $BaSO_4$.

V. 0.7638 gram gave, on ignition, 0.2695 gram $BaSO_4$.

Calculated for $Ba(C_4HBr_2O_3)_2$.		Found.				
		I.	II.	III.	IV.	V.
C	14.74	14.44				
H	0.30	0.63				
Ba	21.04		19.95	20.82	20.77	20.74

This salt is readily soluble even in cold water, and soluble also in alcohol. On boiling its aqueous solution, the decomposition described above ensues, with the evolution of carbonic dioxide. This reaction has not yet been farther studied.

Argentic Mucobromate, $AgC_4HBr_2O_3$. The silver salt may be made by adding a concentrated solution of argentic nitrate to a solution of the barium salt. Since it is quite soluble even in cold water, it is better to use, instead of the barium, the calcium salt, in order to facilitate washing. It is precipitated in fine, felted needles, which blacken quite rapidly on exposure to diffused light, and are decomposed at once on moistening with alcohol or warming with water; argentic bromide is formed, together with some metallic silver. This substance was dried *in vacuo* for analysis:—

I. 0.3601 gram gave 0.1862 gram AgBr.

II. 0.5640 gram gave 0.2903 gram AgBr.

Calculated for $AgC_4HBr_2O_3$.		Found.	
		I.	II.
Ag	29.59	29.70	29.56

Ethyl Mucobromate. The ethyl ether of mucobromic acid may readily be made by saturating its solution in absolute alcohol with hydrochloric acid, or more conveniently by warming this solution

with concentrated sulphuric acid. If considerable sulphuric acid be used, the ether often crystallizes out on standing in large well-formed crystals, otherwise it is precipitated by the addition of water and washed with a dilute solution of sodic carbonate. The crude product contains impurities which can be removed only by repeated recrystallization from alcohol. This recrystallization is more conveniently accomplished if the moderately saturated solution is cooled to 0°. The ether crystallizes in large, transparent forms of the monoclinic system, which melt at 50–51° and boil at 255–260° with partial decomposition. When slightly warmed it has a pungent, aromatic odor.

The analysis of substance dried *in vacuo* over sulphuric acid gave:

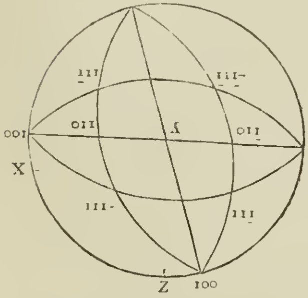
I. 0.8583 gram substance gave 0.7933 gram CO_2 and 0.1686 gram H_2O.

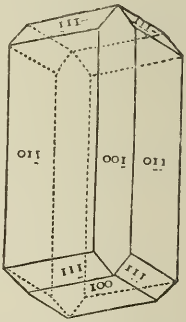
II. 0.7000 gram substance gave 0.6432 gram CO_2 and 0.1377 gram H_2O.

Calculated for $C_4HBr_2O_3.C_2H_5$.		Found. I.	II.
C	25.17	25.24	25.05
H	2.10	2.18	2.18

Mr. Mabery has studied the crystalline form of this substance, and obtained the following results:—

CRYSTALLINE FORM OF ETHYL MUCOBROMATE.





Monoclinic System. — Forms observed, — $\{\bar{1}11\}$ $\{111\}$ $\{100\}$ $\{001\}$ $\{110\}$.

$$a : b : c = 1.053 : 1 : 1.221\ ;\ ac = 78° \ 27'.$$

Angles between Normals.—

	Found.	Calculated.
$\bar{1}\bar{1}1 : \bar{1}11$	82° 11′	Fundamental angles.
$\bar{1}\bar{1}0 : \bar{1}10$	92° 7′	
$\bar{1}11 : \bar{1}10$	32° 56′	
$\bar{1}11 : 001$	64° 53′	64° 46′
$\bar{1}11 : -111$	72° 11′	71° 50′
$001 : -111$	52° 44′	52° 53′
$1\bar{1}0 : -111$	29° 8′	29° 17′
$110 : \bar{1}10$	87° 50′	87° 53′
$110 : 001$	81° 50′	82° 1′
$\bar{1}10 : 001$	98° 4′	97° 59′
$\bar{1}10 : \bar{1}00$[1]	45° 37′	46° 4′

Action of Phosphoric Pentabromide and Acetylchloride.

Mr. O. R. Jackson studied with me the behavior of mucobromic acid towards phosphoric pentabromide and acetylchloride.

Mucobromylbromide. When mucobromic acid is mixed with about four times its weight of phosphoric pentabromide, and the mixture heated for a short time at 110–115°, a quiet reaction sets in, the mass becomes liquid, and water then precipitates a heavy red oil, which after thorough washing with water gradually solidifies at ordinary temperatures, or immediately if cooled to 0°. This substance is very soluble in alcohol, ether, benzol, chloroform, or carbonic disulphide, but crystallizes well from a solution in a little hot alcohol when this is cooled to 0°. After repeated crystallization from alcohol, it forms small, slender prisms, which melt at 55–56°, and have the percentage composition corresponding to mucobromylbromide.

I. 0.6643 gram substance gave 0.3755 gram CO_2 and 0.0374 gram H_2O.

II. 0.2598 gram substance gave 0.4573 gram AgBr.

III. 0.2252 gram substance gave 0.3964 gram AgBr.

	Calculated for $C_4HBr_3O_2$.	Found. I.	II.	III.
C	14.96	15.41		
H	0.31	0.63		
Br	74.77		74.89	74.89

The behavior of this substance towards alkalies is especially

[1] The form { 100 } was observed upon two or three individuals only, and the reflections were imperfect.

characteristic. The reaction may best be observed when baric hydrate is cautiously added to a dilute alcoholic solution. An intense indigo-blue color is at once developed, which, however, soon passes through green to reddish yellow, with the simultaneous formation of a brown-red, flocculent precipitate. The same brown precipitate is formed when the mucobromylbromide is boiled in an excess of baric hydrate ; but the two products which are most characteristic of the decomposition of mucobromic acid under the same conditions, bromacetylen and malonic acid, are formed in such small quantities that they may easily be overlooked. This peculiar behavior led us to suppose at first we had not the simple bromanhydride of mucobromic acid in our hands, but that an hydroxyl group outside the carboxyl had been replaced. A more careful study showed, however, that such was not the case. Although this mucobromylbromide is apparently little affected even by hot water, on boiling it is gradually decomposed, and the solution then contains mucobromic acid (m. pt. 120–121°). Absolute alcohol decomposes it with more difficulty ; still, after several hours' boiling with reverse cooler, on evaporating the excess of alcohol and cooling strongly, crystals separated which had the characteristic form of the ethylmucobromate, and which melted at 51° after recrystallization from alcohol.

Mucobromic Acetanhydride. When mucobromic acid is heated in a sealed tube for several hours with an excess of acetyl chloride at 120°, or when it is heated under ordinary pressure with acetic anhydride, a substance is formed which is very soluble in alcohol, ether, or chloroform, and which may be purified by precipitation by water from its alcoholic solution. It falls as a colorless oil, which gradually solidifies in slender, dendritic needles, which melt at 53–54°.

0.9015 gram gave 0.8050 gram CO_2 and 0.1290 gram H_2O.

	Calculated for $C_4HBr_2O_3.C_2H_3O$.	Found.
C	24.00	24.36
H	1.33	1.59

That the acetyl group enters the carboxyl in this case is shown by the behavior of ethyl mucobromate to acetyl chloride. After several hours' heating, with an excess of acetyl chloride, at 140–150°, the ether was found to be unaltered. The substance which was obtained crystallized in the form of the ethyl-ether, melted at 50°,

and upon analysis proved to contain the required percentage of bromine.

0.2720 gram gave 0.3600 gram AgBr.

Calculated for $C_4HBr_2O_3.C_2H_5$.		Found.
Br	55.94	56.32

Action of Bromine.

Limpricht and Delbrück studied in detail the action of bromine and water upon mucobromic acid, but they made no experiments with dry bromine. It therefore seemed advisable to investigate the action of dry bromine; since the reactions in this case would naturally be less complicated than with aqueous bromine, and on that account might prove to be of more service in determining the constitution of mucobromic acid. In my first experiments I employed equal molecules of bromine and mucobromic acid, but soon found that one molecule of bromine sufficed for the complete decomposition of nearly two molecules of mucobromic acid, although the products of the reaction were essentially the same whether the bromine was used in excess or not.

At 100° very little action was noticeable; at 120–130° the action was marked, but so slow that the temperature was raised to 140°. Here the reaction ran rapidly, and after two hours the bromine had disappeared. On cooling, the tubes were filled with long, prismatic crystals, which were permeated with a nearly colorless oil. On opening the tubes, hydrobromic acid gas escaped in abundance, and with it could be detected a comparatively small amount of carbonic dioxide. The partially solidified product of the reaction was treated with small quantities of cold water. The greater part of the prismatic crystals were in this way carried into solution; while the oil, in which a small quantity of crystals were yet to be seen, was left undissolved. This aqueous solution, upon evaporation, left a white, crystalline acid, very soluble in water, which for purification was converted into the barium salt. Before neutralizing the aqueous solution with baric carbonate, I found it best to evaporate to dryness, and take up a second time with a little cold water, in order to remove the small quantity of undecomposed mucobromic acid which often was present. The barium salt was precipitated several times from aqueous solution by alcohol, and finally crystallized from water by evaporation. Thus purified, it formed brilliant, transparent, rhombic plates, which lost water in desiccator slowly, but which I

was unable to dehydrate perfectly by heat, either at ordinary pressures or *in vacuo*, without causing partial decomposition. The analysis of the air-dried salt gave percentages required by a barium salt of dibrommaleic acid containing two molecules of water of crystallization.

I. 0.8687 gram of substance lost, at 120°, 0.0624 gram H_2O. Of this dried salt, 0.4145 gram gave, by ignition, 0.2341 gram $BaSO_4$.

II. 0.5780 gram of air-dried salt gave, by ignition, 0.3010 $BaSO_4$.

Calculated for $BaC_4Br_2O_4.2H_2O$.		Found. I.	II.
Ba	30.78	30.86	30.63
H_2O	8.09	7.07	

This salt is hardly more soluble in boiling water than in cold; in dilute alcohol, it is almost insoluble. The solubility in water was determined according to the method of V. Meyer.

I. 7.1377 gram of a solution saturated at 19° gave, on evaporation with H_2SO_4 and ignition, 0.2296 gram $BaSO_4$.

II. 6.9649 gram of a solution saturated at 19° gave 0.2249 gram $BaSO_4$.

An aqueous solution saturated at 19°, therefore, contains of the anhydrous salt the percentages:

I.	II.
5.65	5.67

The silver salt could best be made by the precipitation of a solution of the free acid by argentic nitrate. From dilute solution it separated in long, flat needles; from concentrated solutions it was precipitated in small prisms. It proved to be almost insoluble even in hot water. The dry salt exploded violently on heating, or by percussion.

0.6311 gram of the salt, dissolved in dilute nitric acid, gave 0.4859 gram AgBr.

Calculated for $Ag_2C_4Br_2O_4$.		Found.
Ag	44.27	44.22

The lead salt fell as a crystalline precipitate upon the addition of plumbic acetate even to a dilute solution of the free acid.

The acid was liberated from the pure barium salt by the addition of normal sulphuric acid, in quantity insufficient for complete precipitation; the aqueous solution was allowed to evaporate spontane-

ously ; and the acid was then separated from the excess of barium salt by means of ether free from alcohol. Prepared in this way, the acid formed a mass of indistinct, aggregated needles, extremely soluble in water, ether, or alcohol ; and almost insoluble in boiling chloroform, benzol, ligroin, or carbonic disulphide. From a mixture of ether and chloroform it could be crystallized in the form of fine, felted needles.

After standing in desiccator, the acid gave on analysis too high a percentage of bromine (I). It was therefore washed with chloroform, the excess of chloroform evaporated in a paraffine desiccator according to Liebermann's suggestion ; but the percentage of bromine remained essentially unaltered (II). I therefore dissolved the acid in hot water, allowed the solution to evaporate spontaneously, and dried by exposure to the air alone, but failed to alter its composition (III). Subsequently I dissolved the pure anhydride described below in hot water, and found that the acid obtained by spontaneous evaporation of this solution when air-dried also contained more bromine than the formula of the acid required (IV).

I. 0.2050 gram substance gave 0.2860 gram AgBr.
II. 0.2305 gram substance gave 0.3200 gram AgBr.
III. 0.2150 gram substance gave 0.3000 gram AgBr.
IV. 0.2500 gram substance gave 0.3475 gram AgBr.

Calculated for $C_4H_2Br_2O_4$.		Found.			
		I.	II.	III.	IV.
Br	58.38	59.37	59.08	59.38	59.15

From these experiments it would appear that the acid, even at ordinary temperatures, is partially converted into its anhydride. This change goes on rapidly at temperatures near 100°, so that it is impossible to obtain constant melting points. The preparations analyzed melted at 120–125° when warmed with ordinary rapidity. The acid was but slightly volatile with steam, but could be distilled with greatest readiness with the vapor of concentrated hydrobromic acid.

From this acid the anhydride could be obtained without difficulty in a pure state, by heating to 120° in a current of dry carbonic dioxide. The sublimation began at 100°, or possibly lower, but became rapid at 115–120°. The anhydride condensed in lustrous, flattened needles, which melted at 114–115°. In cold water it dissolved but slowly ; in alcohol, ether, benzol, ligroin, chloroform, or carbonic disulphide, it was readily soluble.

I. 0.3672 gram gave 0.2510 gram CO_2 and 0.0010 gram H_2O.
II. 0.2630 gram gave 0.3870 gram AgBr.

Calculated for $C_4Br_2O_3$.		Found. I.	II.
C	18.75	18.65	
H	—	0.02	
Br	62.50		62.61

The aqueous solution obtained by treating the original product from the action of bromine with cold water, therefore, contained mainly an acid of the composition of dibrommaleic acid.

In the mother liquors from the baric dibrommaleate there appeared to be a trace of a more soluble barium salt beside baric bromide; but its quantity was too small to admit of separation and analysis.

The oily residue left undissolved by water gradually solidified upon standing. Cold chloroform dissolved the greater portion of it, leaving a small quantity of short, prismatic crystals. Upon evaporation of the chloroform, an oil was left, which gradually solidified in masses of radiated prisms, contaminated with a small quantity of an oily impurity whose nature could not further be determined. After several crystallizations from alcohol, this substance melted at 55–56°, and when treated with baric hydrate gave the characteristic reactions of mucobromylbromide. It was still further identified by analysis.

0.2280 gram substance gave 4000 gram AgBr.

Calculated for $C_4HBr_3O_3$.		Found.
Br	74.77	74.68

The prismatic crystals, which were sparingly soluble in cold water and chloroform, were recrystallized from hot water, and showed then the characteristic properties of ordinary dibromsuccinic acid. On heating, they remained unaltered till the temperature had risen to over 200°; at a somewhat higher point they had completely volatilized. The sublimate condensed in the colder portions of the tube in oil drops, which gradually solidified. The melting point of the solid thus obtained, after pressing with filter paper, was found to be 126°. According to Fittig and Petri,[1] the sublimate formed under the same conditions from dibromsuccinic acid has the

[1] Ann, Chem. u. Pharm. **195**, 58.

melting point of monobrommaleic acid (128°). The quantity of dibromsuccinic acid formed in this reaction was quite small.

0.2855 gram substance gave 0.3880 gram AgBr.

Calculated for $C_4H_4Br_2O_4$.	Found.
57.97	57.83

When the original product of the reaction was treated at once with dry chloroform, the greater part was instantly carried into solution; and the dibromsuccinic acid, together with a small quantity of mucobromic acid, were left undissolved. The filtered chloroform solution, when shaken with a few drops of water, gradually solidified with separating crystals of dibrommaleic acid; so that the original product must have contained the dibrommaleic acid as anhydride.

The two main products of the reaction were, therefore, dibrommaleic anhydride and mucobromylbromide. The relative weights of these two products were such as to suggest at once the equation:

$$2C_4H_2Br_2O_3 + Br_2 = C_4H_2Br_2O_4 + C_4HBr_3O_2 + HBr,$$

when the dibrommaleic acid would readily pass into its anhydride. The weights obtained in successive preparations were, however, found to vary so much that I am inclined to consider the anhydride as the direct product of the reaction, and the mucobromylbromide a secondary product formed by the action of the hydrobromic acid set free. In either case, the formation of dibromsuccinic acid can hardly be explained without assuming a reducing action of the hydrobromic acid, like that which is normal to hydriodic acid. Although reductions of this sort by the action of hydrobromic acid have seldom been noticed, the conversion of tartaric acid into monobromsuccinic acid by this means, noticed by Kekulé[1] in 1864, would seem to be perfectly analogous.

[1]Ann. Chem. u. Pharm. **130**, 30.

(*To be continued.*)

CHLORO-BROMIDE OF LEAD.

By Malvern W. Iles.

In the treatment of the Leadville carbonate ores by the blast furnace, the writer has noticed a number of very curious and interesting compounds. The facilities here offered for an extended observation are unusually good, inasmuch as the Grant Smelting Co. works have a capacity for treating no less than 150 to 200 tons of ore per day, and an opportunity is offered for collecting furnace products from seven different furnaces.

A compound having the formula Pb(BrCl) has recently been discovered, occurring as a furnace product, in small (2½ inch) circular openings, in the cast-iron supporting plate 11½ inches above the water-jacket. The iron ring rests upon four cast-iron columns, and supports the sheet-iron fire-brick lined structure above. This ring-plate is perforated by holes, which serves to prevent a total rupture of the plate by the expansion caused by the internal heat.

The courses of fire-brick at the boshes close these holes from below, whilst the interior fire-brick lining covers these circular openings, thus forming a small condensation chamber in which the chloro-bromide of lead was found.

As neither Dana nor Naumann makes mention of this compound, and we have been unable to find any description given in any work at our disposal, we feel justified in stating such physical and chemical observations as we have noticed in our investigation.

In order to see whether this compound was contaminated with any silver salt, it was assayed, $\frac{1}{10}$ assay ton yielding by cupellation only a most minute trace. Hence it is to be concluded that this was simply an accidental occurrence of a small amount of ore, or a trace of a volatile silver salt.

We have recently noticed that the white fumes that condense upon the surrounding cool objects in the vicinity of the slag taphole yield 3½ ounces of silver per ton; hence it is not improbable that there is some volatile compound of silver not clearly identified, and which slightly mingles with the chloro-bromide of lead.

Properties.

The furnace crystals occurred in several forms, as for example, in pure white, delicate, dendritic plates, not unlike crystals of lead

chloride; in long acicular needles, in semi-fused distorted needles having a slightly yellowish tint, and also in entirely fused warty masses.

It dissolves in warm water, forming a milky white turbidity which readily clears up on the addition of a few drops of nitric acid. The aqueous solution deposits plate-like crystals, and from the moderately dilute solution, by slow crystallization, one may obtain doubly terminated acicular needles, considerably thickened in the central portion.

It sublimes on charcoal, giving a white coating. In a closed tube it melts readily to a bright red color; upon cooling it lightens up, changing from a lemon yellow to a pure white. On increasing the heat it sublimes in heavy oily drops. Density 5.741.

This product is found to be very stable, and is decomposed by boiling concentrated sulphuric acid, only by repeated applications, and the complete transformation into a sulphate is difficult.

ANALYSES. *Chlorine + Bromine.*

.559 gram	salt gave	.573 gram (AgBr+AgCl)	= 35.714	per ct. (Br+Cl)
1.251 "	" "	1.2825 " "	= 35.718	" "
1.251 "	" "	1.277 " (fused) "	= 35.566	" "
Average of three determinations,			35.666	" "

Lead.

.559 gram	salt gave	.513 gram $PbSO_4$	= 62.695	per cent. Pb.
1.086 "	" "	.996 " "	= 62.717	" "
1.251 "	" "	1.167 " "	= 63.729	" "

The first and second determinations were made upon the furnace product, while the substance used for the last determination was the result of purification by crystallization from an aqueous solution.

Bromine.

1 gram fused (AgCl+AgBr) gave a loss on passing dry pure chlorine gas over the salt, in a bulb tube, of .141 gram = .595055 gram AgBr = 25.321 per cent. Br.

The formula Pb(BrCl) requires Pb=64.186 per ct. and (Br+Cl) = 35.814 per cent. We may state our results as follows:

	Found.		Calculated.
Pb	63.729 per cent.	Pb	64.186 per cent.
Br	25.321 "	Br } Cl	35.814 "
Cl	10.345 "		
	99.395		100.00

The mixed silver salt was readily prepared by making an aqueous solution (aided by a few drops of nitric acid), and adding silver nitrate; after purification by washing with hot water the salt was dried and analyzed. 0.570 gram (AgCl+AgBr) was mixed with pure granulated lead and cupelled in the assay muffle, of course after scorification, and the usual precautions taken for rich chloride ores. The weight of the silver button was .36345 gram, which corresponds to 63.763 per cent. silver; theoretical percentage for formula = 65.158 per cent.

A chloro-bromide of silver, or embolite, has been described and analyzed by Prof. Th. Richter[1] which closely corresponds to the above compound, termed *megabromite* by Breithaupt.

Prof. Richter's analyses gave Ag=64.19 per cent., Br=26.49 per cent., Cl=9.32 per cent. The ratio of the bromine to the chlorine 1 : 0.8, whilst we found in the compound under consideration a ratio of 1 : 0.92.

Inasmuch as the furnaces from which the chloro-bromide of lead was collected had been in blast for some time, it is reasonable to conclude that the chloro-bromide of silver existing in these ores has the same general composition as shown in the above haloid silver salt. While we do not deny the probability that the chloro-bromide of lead may have existed in the ores as such, yet it can readily be seen how a decomposition may have taken place in such a manner as to produce this lead salt, since it is a well known fact that heated metallic lead will decompose all known salts of silver. In conclusion we may state that samples of this compound have been forwarded to Professors Richter, Dana, Remsen, Chandler and others.

[1] Berg- und hüttenmännische Zeitung, **18**, 449.

CHEMICAL LABORATORY, GRANT SMELTING CO., LEADVILLE, COLORADO.

Laboratory Notes from the University of Cincinnati.

XIX.—ALKALIMETRY WITH PHENOL PHTHALEIN AS INDICATOR.

By R. B. Warder.

The properties of phenol phthalein, including the magnificent red color which it yields with alkalies, were described by Baeyer[1] in 1871; but Luck[2] seems to have been the first to use it as an indicator. With caustic alkalies the delicacy of the reaction is marvelous; but when carbonates are present, the change of color takes place more gradually, and cold solutions of an acid carbonate are not colored at all. Even the carbonic acid of the atmosphere may have a marked influence.

For the following experiments a weighed quantity of a dark colored sample of phenol phthalein from Kahlbaum was dissolved in weak alcohol, and a roughly graduated dropping tube was inserted in the stopper of the flask containing the solution, by which any required quantity of the indicator could be approximately measured out. 0.1 milligram of commercial phthalein was added to 100 cc. distilled water, and $\frac{1}{100}$ normal NaOH solution was run in from a burette. With 0.4 cc. $\frac{1}{100}$ n. alkali, the color was barely perceptible; with 1 cc. it was distinct, with 2 cc. a beautiful faint pink color was produced, which deepened to a distinct crimson red with 4 cc. of the alkali. The color produced by one or two cc. could easily be discharged by shaking with air, and that produced by 4 cc. was entirely discharged by less of my own breath than a single expiration; indeed, this experiment is well adapted for lecture demonstrations of the carbonic acid of the breath, being much more striking than the usual lime-water test. With different samples of ordinary distilled water, a varying amount of alkali was required to produce the succession of tints above described; the first appearance of color is often very transient. The least quantity of alkali is required with water from which the carbon dioxide has been carefully expelled by heat, and it is convenient to have a supply of such water at hand in a well stoppered flask.

As a further test of the delicacy of this indicator, 20 cc. of $\frac{1}{2}$

[1] Ber. d. ch. G. **4**, 658.

[2] Zeitsch. anal. Chem. 1877, 332.

normal alkali were carefully neutralized with oxalic acid (with boiling to expel CO_2), then diluted to about 100 cc., and with the aid of 0.4 milligram phthalein a distinct tint was produced by the addition of 1 cc. of $\frac{1}{100}$ normal NaOH, and a beautiful pink color by less than 2 cc. Hence, a variation of less than 0.1 per cent. of the whole quantity of alkali used produced a marked change even in very dilute solution; with concentrated solutions the delicacy is much greater.

On adding acid to a cold dilute solution of sodic carbonate we may suppose the first reaction to take place thus:

$$2Na_2CO_3+C_2H_2O_4=C_2Na_2O_4+2HNaCO_3;$$

and as a solution of $HNaCO_3$ gives no color with phthalein until it is decomposed by heat, we might expect the reddened solution of a carbonate to be entirely decolorized by $\frac{1}{2}$ equivalent of acid. I have been able to realize this expectation only in part, yet the facts indicated serve as a basis for a method for the estimation of causticity of solutions which do not contain too large a proportion of carbonate. The alkaline solution, with a suitable quantity of phenol phthalein, is mixed with standard acid, in the cold, until the red color either vanishes entirely, or (if the reaction is lacking in sharpness from the presence of carbonate) until the color is extremely faint. Of course the solution must be sufficiently dilute to avoid any danger of effervescence in this first titration. The changes of tint closely resemble those observed when a solution of rosaniline is greatly diluted, and it is a valuable aid to the eye to keep such a solution at hand for comparison; and as the depth of color at this stage varies with the quantity of indicator used, it is desirable to take some definite amount. After completing the first titration, the mixture is boiled thoroughly with successive additions of more acid, until the last returning trace of red color is discharged by a single drop; or the end may be more quickly reached (in accordance with the law of the "action of mass") by boiling at once with excess of acid, and completing the titration with the aid of caustic alkali. The end reaction in this case, which is very sharp, is marked by total discharge of color.

Let A_1=the acid required in first titration, and A_2=that required in the second, with any needed deduction for the alkali used near the end; then A_1+A_2 represents the total alkali; $A_1—A_2$ represents the caustic alkali; $2A_2$ represents the carbonate.

The following titrations were made to test this method. Solutions used were: A, oxalic acid, 0.991 normal; B, standard sodic carbonate, ½ normal; C, sodic hydrate, nearly ½ normal. 0.2 milligram phenol phthaleïn was used in each case.

The caustic soda was prepared by dissolving metallic sodium in water from which the carbon dioxide had been expelled. It was kept in a vessel provided with soda-lime ventilator, and was drawn without contact with the laboratory atmosphere, through the lower end of an ordinary burette, which was also provided with a soda-lime ventilator at the top.

Notwithstanding these precautions, a trace of carbonate appeared to be present in solution C, or to be formed during titration; for 42.22 cc. of C were exactly decolorized in the cold by 21.39 cc. of A; on boiling, the color returned, and a further addition of .06 cc. of the acid was required. By the formula given above, the caustic alkali present represents $21.39 - .06 = 21.33$ cc. of A, or 21.14 cc. of perfectly normal acid. Hence we may assume that its strength in NaOH is $1.0014 \times \frac{1}{2}$ normal with an admixture of Na_2CO_3 in the quantity used, equivalent to $2 \times .06 = .12$ cc. of normal solution. Various mixtures of B and C were then titrated in the same manner. The following table expresses the volumes of these solutions used, as measured from burettes. A_1 is the quantity of acid required in the first titration, A_2 is the additional amount required when the solution was boiled:

	B	C	A_1	A_2	A_1+A_2	A_1-A_2	$2A_2$
(1)	2.53	41.70	21.71	.69	22.40	21.02	1.38
(2)	4.90	39.65	21.33	1.30	22.63	20.03	2.60
(3)	9.85	38.04	21.74	2 56	24.30	19.18	5.12
(3′)	"	"	21.80	2.50	"	19.30	5.00
(4)	10.61	38.23	22.12	2.64	24.76	19.48	5.28

The following table shows the total alkali, the caustic alkali and the carbonate taken, as represented in columns B and C, together with the corresponding quantities found by means of A_1+A_2, A_1-A_2 and $2A_2$. For convenience, these quantities are not calculated by weight, but are represented in cc. of normal solution, as the object is merely to exhibit the experimental errors incident to this method. It is allowable to assume, in calculating these results, that each portion of C used contained the same quantity of Na_2CO_3 that was found in the preliminary titration:

	Total Alkali.		NaOH.		Na_2CO_3.	
	Taken.	Found.	Taken.	Found.	Taken.	Found.
(1)	22.25	22.20	20.86	20.83	1.38	1.37
(2)	22.41	22.43	19.84	19.85	2.57	2.58
(3)	24.08	24.08	19.03	16.01	5.04	5.07
(3′)	"	"	"	19.13	"	4.96
(4)	24.55	25.54	19.13	19.30	5.42	5.23

Two values of A_1 and A_2 are given for the third experiment. Those in line (3) correspond to a reading taken, while there was still a faint reddish tinge, while (3′) represents a complete discharge of color in the first titration. The difference is not great, but a little practice will enable the operator to obtain still closer results. In experiment (4) the color was quite inappreciable when the reading was taken ; and the result shows that A_1 was rather too large and A_2 too small.

The use of phenol phthalein as an indicator, so strongly recommended by Luck, seems to have been somewhat neglected in consequence of the very property which is the basis of the method just described for distinguishing alkalinity and causticity. I think the convenience and accuracy of the new method will recommend it to those who have occasion to make such determinations : but, as its capabilities are not yet exhausted, I hope to continue the investigation, and ascertain whether the plan can be modified for the detection and estimation of carbonic acid in general.

March 10, 1881.

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

[*Continued from Vol. 2, p.* 426.]

Artificial Production of Heat for Domestic Purposes.

The manufacture of artificially compressed blocks of solid fuel from the otherwise waste bituminous coal which has been crushed to dust in the process of extraction, has been largely extended of

late years, though the proportion of such fuel in use is small as compared with other materials.

The cheapest form of liquid fuel—crude petroleum—has been tried in many forms of stoves and burners, for warming of rooms, cooking, and other domestic purposes, but the difficulty of securing complete combustion, the consequent odor not only in the neighborhood of the fire, but often attaching itself to articles of food cooked by it, and the serious danger attending the storage, pouring, and use of such a liquid in unskilled hands, have proved themselves objections sufficient to prevent any general or very extensive adoption of this heating agent. Its true field of future use, notwithstanding the limited success which has hitherto resulted from experiments in this direction, seems likely to be found on board armored war vessels as the source of motive power beneath the boilers of marine engines; its great heat-producing power for given weight, freedom from ash, sulphur and other impurities, compactness of stowage, economy resulting from the complete control over consumption, the facility and quickness with which the supply may be taken on board or discharged, and other peculiarities, giving it immense advantages over ordinary coal. The like reasons render it not improbable that petroleum-burning locomotives may yet be successfully constructed.

"Water gas" or "hydrocarbon gas," resulting from the reaction of steam upon glowing carbon in some cheap form, shown by Siemens to be producible with great economy by means of his "generator" or analogous arrangements, has been used to some extent for domestic heating, and offers advantages which seem likely to be more generally appreciated in the future than they yet have been. Much remains to be done in working out the details of proper arrangements for storing, distributing and using the vast volumes of such gas which would have to be dealt with if its use should become general in even a single large city, and the possibilities of mischief from its highly poisonous character would require well considered precautions against its escape in an unburnt state, but it may fairly be said that such difficulties are not at the present day nearly so formidable as those which seemed to oppose the introduction of coal gas for illuminating purposes seventy or eighty years ago. The question of using gaseous fuel for domestic heating has assumed new interest of late in London, where the strong feeling anciently entertained against bituminous coal on account of its smoke and "stench," as testified to by royal proclamations, petitions to Parliament, and other public documents in the 15th, 16th and 17th centuries, has been revived amidst the great population over which a gloomy winter atmosphere broods upon the banks of the Thames. The practical ingenuity of Dr. C. W. Siemens has been very recently shown in his suggestion[1] of an efficient form of grate for burning gas, intended and apparently well calculated to

[1] Nature, Nov. 11, 1880, p. 25.

avoid the difficulties which have presented themselves in using such fuel. The price, which may well be called extravagant, paid by consumers of ordinary coal gas in American towns, and even cities, precludes here its use as proposed by Dr. Siemens, but there is no valid reason against the production of generator gas at a cost which would make it a thoroughly economical source of heat. Another suggestion has lately been made as to the suppression of a smoky atmosphere in cities burning bituminous coal, namely, that the whole supply of such coal should be partially coked at a low temperature, so as to obtain a very rich gas for illuminating purposes, with abundant and valuable tar products, leaving a semi-coke behind for use as domestic fuel, which it is assumed might be burned with little or no escape of smoke. This idea seems complicated with many more doubtful conditions than that of adopting for general use the generator gas.

Other important and interesting questions in relation to the future supply of heat to our dwellings must be dismissed as not chemical but physical in their character, such as the distribution to many houses of heat from central stations by means of steam pipes, lately brought into experimental use on a working scale in this country, the transmission of mechanical energy for moderate distances by such contrivances as Hirn's telo-dynamic wire with subsequent conversion into heat, the transmission and conversion of cheap electricity, itself derived from the heat of burning fuel by means of dynamo-electric engines, the more direct storing up and utilization of sun heat, particularly that of low temperature, etc., etc.

For *cooling* the air of dwellings in hot climates the more efficient ice machines of the last twenty years have been to a limited extent resorted to. In addition to the various volatile liquids used singly which have been alluded to in an earlier part of this report as employed in working these refrigerating machines, it has been lately proposed to use a mixture of ether or methyl chloride with sulphur dioxide or ammonia, taking advantage of the solvent action of the former bodies on the latter to work at lower pressures than would otherwise be necessary.

Artificial Production of Light.

Candles.—The two principal directions of advance in the procurement of crude materials for candle-making have for some years been, the importation of larger and larger supplies of vegetable oils and waxes from the hotter regions of the globe, and the more extensive and skilful extraction of fatty matter from waste residues of various sorts. Under the former head palm oil and coconut oil—particularly the former—still hold the first place, but shea butter, carnauba wax, and sundry other materials have come more or less into use.

Under the latter head slaughter-house scraps and refuse, the bodies of dead animals from the streets of cities, condemned meat,

bones to be afterwards used for glue making or for bone-black, the skimmings of liquid sewage, the dirty packing removed from railway axle-boxes, greasy cotton waste which has been used for wiping machinery, soap-water from laundries and private houses, refuse from the clarification of olive and colza oils, etc., etc., have been brought into requisition, and by means of heat, pressure, solution in carbon disulphide or light petroleum hydrocarbons, and treatment with small quantities of acids and alkalies, have been made to yield important supplies of fatty material, partly to be used as such and partly to undergo conversion into pure and clean mixtures of the fatty acids. In the Southern United States the rapid growth of the cotton-seed oil industry is worthy of note, although the product goes largely into use in other hands than those of the candle-maker.

In the important manufacture of the fatty acids the three processes now chiefly in use are, 1st. Decomposition by means of sulphuric acid, and distillation with the aid of superheated steam. 2d. Saponification by lime in closed vessels under pressure, and decomposition of the lime soap by sulphuric acid. 3d. Saponification by lime as before, followed by treatment with a small excess of sulphuric acid, and distillation in a current of superheated steam.

The relative advantages of these processes under different conditions have been discussed by Prof. De Wilde in the Belgian official report upon the Paris Exhibition of 1878. Lime is chiefly used by the smaller manufacturers; sulphuric acid, followed by distillation, in the largest establishments. By far the most interesting novelty in this field of industry is the appearance in the market, introduced by two French manufacturers, of palmitic acid, artificially made from oleic acid by heating with strong potash lye at 300° to 325° C., thus producing potassium palmitate and acetate, to be separated by washing with a limited quantity of water, the former salt to be then decomposed by sulphuric acid. The quantity of caustic potash required is said to be large—twice the weight of the oleic acid to be treated—but it is recovered, the acetate of potassium being calcined and converted into carbonate, to be causticized with lime, while the palmitate is either decomposed by sulphuric acid, as just mentioned, and the sulphate of potassium converted into carbonate by the Leblanc process, or palmitate of calcium is formed by heating with lime under pressure, caustic potash being thus directly reproduced, and the lime salt afterwards decomposed by sulphuric acid. The value of the principal by-product of the fatty acid manufacture, glycerine, constantly increases, as its useful properties are applied in new directions and upon a continually larger scale. As a solvent in pharmacy, in connection with perfumery and various articles of food, as a preservative of animal and vegetable substances from decay, as an ingredient in the manufacture of beer, as the means of keeping moist and soft such articles as chocolate, tobacco and soap, as preserving the pliancy of leather and maintaining the softness and

delicacy of the living skin, as a lubricant, in admixture with water to guard gas-meters against stoppage by freezing, as the material for making nitro-glycerine, and in sundry other directions this substance, twenty-five years ago but little known or used, has acquired an important place in general consumption. While its price has been greatly lowered, the state of purity in which it is placed upon the market has been improved until now there is little left to be desired in this regard.

The manufacture and purification of solid paraffine have rapidly developed, and new sources of supply have been resorted to. The comparatively small proportion of such solid hydrocarbons existing in the thinly fluid petroleum of Pennsylvania is in the hands of some refiners carefully collected, by freezing out and pressure, from the heavier lubricating oils, and by regulated washing with petroleum spirit brought to a beautiful condition of whiteness. The thick and heavy petroleum of the Caspian and of Burma is largely worked, and yields a much more considerable product, and the ozokerite of Austrian Gallicia has for the last twenty years added greatly to the general supply of analogous material, the purified "ceresine" obtained from it justifying the name by a nearer resemblance to beeswax than is presented by any other such material of mineral origin. The great hardness and high fusing point of this mineral wax when it has been simply purified are remarkable and valuable; when the crude material is submitted to distillation, products more nearly resembling the true paraffines of the C_nH_{2n+2} series are obtained. Furthermore, the production of paraffine for candle-maker's use by destructive distillation of such materials as Boghead coal, certain lignites, such as the Schweelkohle of Saxony and Thuringia, and bituminous shales, is carried on with success, serving to continue the use of these crude substances beyond the time at which their distillation for liquid illuminants would have ceased to be profitable.

Incidentally may be mentioned here the recent growth of the manufacture, and wide extension of the use, of such semi-solid products as are sold under the names "vaseline," "cosmoline," etc., derived from the later residues of petroleum distillation, and in purified form intended to serve as substitutes for lard and other fats in the preparation of salves and ointments, in dressings for surgical and veterinary practice, as a vehicle for perfumes in making "pomades" for the hair, and as an application to leather with a view to preserve its flexibility. The objection arising from petroleum-like odor has been successfully removed, and the insusceptibility of these products of rancidity gives them real value.

Liquid Illuminants for burning in Lamps.—Doubtless no natural substance has been within the last twenty years added to the world's store of crude materials equal in importance to liquid petroleum. Immense as the supply has previously been from the United States, it has for the last two or three years not only shown no sign of falling off, but has actually exhibited an enormous

increase. Among foreign sources of supply the Russian petroleum region of the Caucasus has acquired greatly increased commercial importance. In regard to the product from this district the interesting fact seems lately to have been made out that it consists largely of a mixture, not of true paraffines, nor of members of the olefine series, but of hydrocarbons, isomeric with the latter, which may be viewed as addition derivatives of the aromatic series, such as C_6H_{12}, etc. The same may be true of the Gallician ozokerite, which is said to afford the empirical formula C_nH_{2n}, and, in very small quantity, these aromatic hydrocarbons have also recently been detected in American petroleum. The refining of petroleum is a comparatively simple process, but has been improved in details, and in the care with which these are carried out, so that the best "kerosene" for burning is a beautifully colorless, clear, limpid liquid. The chief desideratum for the refiners is the discovery of a sufficiently extensive use for the lighter and more volatile products of distillation, known as "petroleum spirit," "gasoline," "benzine," etc. Although these materials have come largely into use as solvents and for some other purposes, their consumption is still insufficient to absorb profitably the immense quantities produced. Hence the temptation to allow an undue proportion of the highly volatile hydrocarbons to remain in commercial kerosene, to mix the two after they have been separated by distillation, and even to substitute the former for the latter under various flimsy pretences of rendering the material "inexplosive." Much ingenuity has been bestowed upon the various devices for testing the safety of kerosene oil, and minute instructions have been drawn up for their use, but, although the process is essentially a very simple one, it requires practice, an honest desire to obtain trustworthy results, and above all a clear comprehension of the chemical and physical principles involved. Great improvements have been made in lamps, particularly in those intended for burning petroleum, the shape and proportions of the burners and chimnies being much superior to those of the earlier lamps used for this illuminant.

Illuminating Gas.—There has been no radical change for some time past in the method of manufacture of ordinary coal gas. Where systematic public inspection is practiced, the production of gas of higher illuminating power, and in the hands of those aiming at improvement, the tendency to more careful purification, and better utilization of by-products, have been chiefly noticeable. The Laming mixture, in which ferric hydrate is the principal ingredient, has passed into more extensive use in the purifiers than formerly, though lime is still employed. Liebermann has recently suggested a new mode of removing the vapor of carbon disulphide, which tends so obstinately to remain in the gas under existing systems of purification,—namely, by taking advantage of the eagerness with which this vapor is absorbed by solid paraffine, which may be used in the crude state, and from which the carbon disulphide may be easily recovered by distillation. It would be important to ascertain

whether the luminiferous hydrocarbons would not also be absorbed to such an extent as materially to lower the value of the gas ; that benzole, which Berthelot has found to be the chief illuminant in Parisian gas, is so absorbed by paraffine is stated by Liebermann himself. The suggestion has already been noticed that the whole of the bituminous coal used in English cities as fuel should be subjected to incomplete destructive distillation at low temperatures, so as to leave a kind of coke assumed capable of burning without objectionable smoke, while very rich illuminating gas would be obtained in great abundance. The great disturbance of values for the solid fuel residue, the gas, and the tar products, which carrying out such an idea would entail, makes it difficult to form even an approximate estimate of the net economic result. Very real improvement has been made within the last few years in the arrangements for using coal gas, notably as regards the details of construction of the burners, and the due regulation of the pressure under which the gas escapes.

Pettenkofer has shown how gas of fair illuminating quality may be made from wood or peat, by distillation at quite low temperature, and carrying the volatilized products through a second retort or "generator" at much higher temperature.

Crude petroleum has been employed by various inventors as material for the production of permanent gas, but its use cannot be said to have got beyond the field of experiment.

The production of "water-gas" by bringing steam in contact with red hot solid fuel, and afterwards rendering luminous the gaseous mixture so produced by causing it to take up the vapor of some of the heavier hydrocarbons, has been many times revived in more or less improved forms, and of late with a very notable measure of economic success.

In the United States the combustion from ordinary gas fixtures of the most volatile portions of petroleum-gasoline, or light petroleum spirit—carried along as vapor by a current of air produced by simple mechanical contrivances—has been brought extensively into use, but the results are far from satisfactory, both on account of the danger attending the handling the gasoline itself by ignorant people, and from the annoying variability of the extent to which the vapor is formed or condensed under varying conditions of atmospheric temperature. The comparatively high density of the hydrocarbon vapor is a further disadvantage, as invisible trains of combustible material are liable to be formed from burners left open but a short time, which may blaze up dangerously from lights placed at a much lower level.

The valuable process of Tessié du Motay for cheaply preparing oxygen gas, and the various modes of using it in connection with illumination, whether by throwing jets of mingled oxygen and hydrogen or "water-gas" upon pencils of refractory solids, or by introducing oxygen into hydrocarbon flames rich in carbon, have not established themselves in general use, but are still capable of being occasionally resorted to, with advantage, under special conditions.

Illuminating gas compressed to a tension of about six atmospheres in tinned iron cylinders has come into use as the most convenient means of rendering gas lighting portable, as in railway carriages, on board steamships, &c.

It is needless to say that the greatest amount of interest in questions of illumination has of late attached to the use of electricity, applied either to the production of the "galvanic arc," or to maintaining the incandescence of a slender rod of carbon or other refractory material. Although the most important features of the problem of electric lighting are of purely physical character, not suitable for discussion in this report, some minor matters of chemical interest have from time to time been brought forward. A noteworthy example of mixed chemical and physical principle is afforded by the recently invented Maxim lamp, in which the integrity of the slender strip of incandescent carbon is secured, at any rate for a long time, by enclosing it, not in a vacuum, but in an atmosphere of gasoline vapor, the deposition of carbon from which tends to strengthen the parts of the slip originally weakest by these becoming most strongly heated at first. It may be remarked in passing that probably no subject of scientific and industrial interest has, for a long time, been so much discussed in public as electric lighting, with such remarkable neglect of the most fundamental and simple principles involved, both of scientific truth on the one hand and of economic conditions on the other; and this has in many instances been true, not only of mere newspaper discussion and common conversation, but of the utterances of men who ought not to have been ignorant of, and presumably were not ignorant of, the considerations they neglected.

As an interesting and practically valuable contribution to our methods of obtaining light under special conditions may be mentioned in conclusion the "luminous paint" patented by Balmain, and lately brought into the market by Ihlee and Horne of London. This revival in industrial form of the "phosphori" which attracted so much attention from the chemists of the 17th and 18th centuries seems destined to a really useful place in the service of man in the future, though the extent of its utility can perhaps hardly yet be foreseen. The principle of its light-storing power is physical, but the actual production of the sulphide of calcium, which seems to be the essential material used, is a process of chemical manufacture.

Appendix to Production of Heat and Light.—Matches.

In the production of these useful little articles the use of round splints of wood, made by end-on compression of wood through a perforated steel block, has for many years generally replaced the rougher sawn or cleft splints, at any rate for all but the coarsest matches, and for the preliminary tipping sulphur is seldom now employed, its place having been taken by stearic acid or paraffine.

Red or amorphous phosphorus, after having for a time been in-

troduced to a considerable extent into the composition of the principal tipping, has been pretty generally abandoned in favor of the longer known, cheaper, and more easily combustible crystalline form of the element. In the composition used in making some of the Swedish matches, potassium pyrochromate furnishes a portion of the oxygen along with the more active chlorate or nitrate of potassium.

"Safety matches," capable of being ignited only by friction upon a specially prepared surface, may be counted as a comparatively recent branch of the manufacture; the active materials used being generally antimony sulphide or sulphur and potassium chlorate on the match, and amorphous phosphorus with pulverized glass on the surface of the box. At the Philadelphia Exhibition of 1876, safety matches of American manufacture were shown which dispensed altogether with the use of phosphorus, the match being tipped with a composition containing sulphur, red lead, and potassium chlorate, while the prepared surface on which it was to be struck consisted of hard vulcanite with which a large proportion of antimony sulphide had been incorporated.

J. W. MALLET.

(*To be continued.*)

REPORT ON ANALYTICAL CHEMISTRY.

[*Continued from Vol.* 2, *p.* 204.]

Oxygen.—As previously reported,[1] Tiemann and Preusse, in their comparative examination of the three methods usually employed for the determination of the oxygen absorbed by water, found that the results obtained by the method of Bunsen and that of Schützenberger were nearly concordant, while those obtained by the method of Mohr were uniformly too low. These conclusions were not in accord with those reached by J. Koenig and L. Mutschler,[2] who stated that the methods of Bunsen and Mohr yielded closely agreeing results, and recommended that the method of Schützenberger be discarded. The objections to the method were: 1. The instability of the standard solution of hydrosulphite; 2. The want of uniformity in its action upon free oxygen contained in water and upon the oxygen of ammoniacal cupric and iron-alum solutions by means of which it is usually standardized; 3. The want of uniformity in its action in aqueous solutions of oxygen of different degrees of concentration.

Koenig and C. Krauch[3] have now published the results of a reinvestigation of the subject. Their conclusions are: 1. That the absorption coëfficient of air for distilled water as determined by Bunsen, which has hitherto been relied upon as the standard for

[1] This Journal, 2, 67. [2] Berichte d. deutsch. chem. Gesell. 10, 2017.
[3] Zeitschrift analyt. Chemie, 19, 259.

testing the correctness of the results obtained by the different methods, is not in all cases to be depended upon; 2. That the method of Mohr gives results which are uniformly too high, instead of too low as stated by Tiemann and Preusse; 3. That, contrary to the conclusions of Tiemann and Preusse, the method of Schützenberger gives results which are always too low; 4. That, though neither the method of Mohr nor that of Schützenberger gives absolutely correct results, either can be successfully employed to determine the relative amounts of oxygen contained in different waters. But if the latter is used, the hydrosulphite solution must be standardized by means of an aqueous solution of oxygen of known concentration and not by means of an ammoniacal cupric or an iron-alum solution.

Ozone.—Em. Schoene[1] calls attention to the fact that, since the existence of hydrogen superoxide in the air has been demonstrated, the occurrence of ozone as a constituent of the atmosphere has become very doubtful. Most of the reactions formerly relied upon for the detection of ozone are also produced by hydrogen superoxide. The latter liberates iodine from the iodides and oxidizes thallous compounds. It does not oxidize manganous salts, but such oxidation cannot be regarded as an evidence of the presence of ozone, since ordinary oxygen in the presence of carbonate of ammonium—which is always to be found in the air—will effect it. The tarnishing of silver may be, and probably always is, due to the presence of sulphides. The odor sometimes observed and ascribed to ozone is at best a questionable argument for its presence. Most observers would be liable to confound the odors of ozone and hyponitric acid. Moreover, ozone is not produced by the electric spark in a mixture of oxygen and nitrogen, but only oxide of nitrogen, hence the fact of visible electric discharges in the air is no evidence of its formation. It is produced by the silent discharge, but of this, as an atmospheric phenomenon, we still know too little to justify us in regarding it as a probable source of supply.

Water.—Fr. Rüdorff[2] has described a simple and convenient apparatus for the determination of the aqueous vapor of the air by absorption. It consists of a flask of the form of an ordinary triple-mouthed Wolff's bottle, and has a capacity of about 1000 cc. Each of the three apertures is fitted with a ground glass stopper. One of these stoppers carries a bent glass tube which serves as a manometer, another a finely graduated burette for sulphuric acid, and the third a glass tube to connect the interior of the flask with the outside air. The manometer, burette and glass tube each contain a glass stopcock situated just above that portion of them which forms the stopper. The liquid used in the manometer is sulphuric acid having a specific gravity of 1.3, which, at ordinary temperatures, neither gives up nor absorbs an appreciable amount of water. The burette is filled with concentrated sulphuric acid. To deter-

[1]Berichte d. deutsch. chem. Gesell. **13**, 1503. [2]Ibid. **13**, 149.

mine the aqueous vapor in any specimen of air filling the apparatus, the stopcocks of the manometer and the glass tube are closed, that of the burette opened and a small quantity of sulphuric acid allowed to flow in. The stopcock belonging to the manometer is then opened, whereupon the dilute sulphuric acid rises in the limb nearest to the flask in consequence of the diminished internal pressure. Lastly, sulphuric acid is added from the burette until equilibrium is restored in the manometer. The volume of sulphuric acid used is equal to the volume of aqueous vapor originally present.

Other, but certainly not superior, forms of apparatus for the estimation of aqueous vapor by absorption have been proposed by A. van Hasselt[1] and A. Matern.[2]

Hydrogen Superoxide.—Em. Schoene[3] recommends the use of thallium papers for estimating the "oxidizing principle" of the atmosphere, which, since the existence of ozone in the air has become doubtful, he believes to consist mainly and perhaps wholly of hydrogen dioxide. The oxidation of the thallous compounds is not dependent on the presence of moisture. Moreover, the oxidized papers can, with proper care, be preserved for any length of time and thus afford a visible record of observations made. They are best prepared by saturating, not more than two or three days before use, strips of Swedish filter paper with a solution containing in each 100 cc. 10 grams of thallium hydroxide, and drying as quickly as possible in the air. They are then preserved until wanted in closed vessels over burned lime. The defects of the methods of observation which depend upon the liberation of iodine from iodide of potassium (Schoenbein's and Houzeau's), are such, he thinks, as to render them wholly unfit for use. The quantity of iodine liberated depends upon the amount of moisture present, hence the "ozonometer" of Schoenbein, as can be demonstrated, is nothing but a crude hygrometer; also upon the hygroscopic condition of the materials employed in preparing the papers, hence papers obtained from different sources, though prepared in the same manner, are unequally affected when exposed together under the same conditions.

Halogens.—In order to obtain a nearly constant current of hydrochloric acid gas, L. L. de Koninck[4] uses solid chloride of ammonium and concentrated sulphuric acid. The same author[4] recommends for oxidizing purposes a solution of bromine in water, containing ten per cent. of bromide of potassium.

According to A. Jorissen,[5] minute quantities of iodine in bromine may be detected by the following method: A few drops of the bromine to be tested are placed in a porcelain dish, 30 cc. of a cold saturated solution of chlorate of potassium added, and heat applied until all color has disappeared. After cooling, the solution is

[1] Zeitschrift analyt. Chemie, **19**, 67. [2] Pogg. Annalen, N. F. **9**, 147. Also **10**, 149.
[3] Ber. d. deutsch. chem. Gesell. **13**, 1508. [4] Zeitschrift analyt. Chemie, **19**, 467, 468.
[5] Ibid. **19**, 353.

treated with a few drops of a solution of sulphate of morphine (prepared by dissolving 0.5 gram of morphine in an excess of dilute sulphuric acid and diluting to 50 cc.) and a little chloroform. If iodine is present, a violet color will be imparted to the chloroform. To test bromide of potassium for iodine by the same method, the solution of the bromide is first treated with two or three drops of pure bromine water. To determine the halogens in chlorates, bromates and iodates, F. Fleissner[1] boils the solutions containing them for an hour with an excess of zinc dust. The reduction is complete. In the case of chlorates only is it necessary to acidify with acetic acid. Perchlorates are not reduced by this treatment.

Nitrogen.—W. H. Perkin[2] uses a mixture of precipitated manganic oxide and chromate of potassium to remove the oxides of nitrogen formed when nitrogenous organic compounds are burned for the purpose of determining carbon and hydrogen. The mixture fills from four to six inches of that portion of the combustion tube usually occupied by metallic copper, and, if the temperature is kept sufficiently low (200°–250°), will completely absorb and retain any oxides of nitrogen formed. The author recommends, in view of the fact that manganic oxide may contain alkali, the use of a chromate containing about 10 per cent. of bichromate. Mixtures of chromate and oxide in the proportions of 1 : 2 and 2 : 1 were employed in the experiments described. The mixture will also absorb sulphuric and sulphurous acids, but the temperature required is higher than the retention of the nitrogen compounds will admit of. A difficulty which would, therefore, present itself when an organic compound containing both nitrogen and sulphur is burned with oxide of copper might be obviated by using a larger quantity of the mixture and heating to a high temperature that portion only which is nearest to the substance.

New forms or arrangements of apparatus designed to facilitate the collection and measurement of the nitrogen obtained by Dumas' method have been described by H. Schwarz,[3] E. Ludwig,[4] H. Schiff,[5] K. Zulkowsky,[6] C. E. Groves[7] and W. Staedel.[8] In order that the same combustion tube may serve for several determinations, Zulkowsky and Groves place the material from which the carbon dioxide is to be obtained in a separate tube and connect the two by means of a smaller tube. Zulkowsky recommends surrounding the tube, which serves as a carbon-dioxide generator, with a cylinder of sheet iron, which may be shoved backwards or forwards. In this manner the heat is uniformly distributed and a more constant current of gas obtained.

Arsenic.—L. Mayer[9] determines arsenious acid in the presence of arsenic acid by means of its reducing action upon an ammonia-

[1] Monatshefte für Chemie, **1**, 313. [2] Journ. Chem. Society, 1880, 121, 457.
[3] Ber. d. deutsch. chem. Gesell. **13**, 771. [4] Ibid. **13**, 883. [5] Ibid. **13**, 885. [6] Ibid. **13**, 1096.
[7] Journal Chem. Society, **13**, 500. Also Berichte d. deutsch. chem. Gesell. **13**, 1341.
[8] Zeitschrift analyt. Chemie, **19**, 452. [9] Jour. prak. Chemie, **22**, 103.

cal solution of silver nitrate. The reaction which takes place is represented by the following equation: $As_2O_3+2Ag_2O=As_2O_5+4Ag$.

The arsenious acid or mixture of arsenious and arsenic acids is dissolved in ammonia, poured into a strongly ammoniacal solution of nitrate of silver, and the whole boiled about thirty minutes. The metallic silver may be collected, washed with water containing ammonia and chloride of ammonium and weighed as such, or dissolved and precipitated as chloride.

E. Fischer[1] finds it practicable to separate arsenic quantitatively from the other metals precipitated by sulphide of hydrogen by distilling with ferrous chloride and hydrochloric acid. The material containing the arsenic, if an alloy, is dissolved by means of hydrochloric acid and chlorate of potassium; if a mixture of sulphides of arsenic, antimony and tin, it is prepared by treating the alkaline solution with chlorine. The excess of chlorate of potassium is then nearly destroyed by warming for a short time with concentrated hydrochloric acid. If nitric acid has been used it must be removed by evaporating with sulphuric acid. The solution is placed in a globe-shaped flask holding from 500 to 600 cc., treated with 20 cc. of a saturated solution of ferrous chloride and with 20 per cent. hydrochloric acid until the volume equals about 140 cc. The flask is then connected with a cooler, and the contents distilled until the volume of the residue has been diminished to 30 or 35 cc. If the distillation is continued beyond this point other chlorides may volatilize. If the quantity of arsenic to be removed does not exceed 0.01 gram, one distillation suffices. If more is present, hydrochloric acid must be added to the residue and the distillation repeated. The separation of arsenic from lead, copper, bismuth, cadmium and mercury is complete. The distillate may however contain small quantities of the chlorides of tin and antimony, but their presence does not interfere with the volumetric determination of the arsenic. If the distillate is treated with ferrous chloride and redistilled until the residue has been diminished to 30 cc., the arsenic will be completely freed from both tin and antimony.

Carbon.—T. Weyl and B. von Anrep[2] give the following points for the chemical diagnosis of poisoning by carbon monoxide:

1. The blood is to be preserved in fully filled flasks and kept until wanted for examination in a dark and cool place.

2. If, on addition of sulphide of ammonium or the solution of ferrous-ammonium tartrate of Stokes, no reduction to hemoglobine takes place, carbon monoxide-hemoglobine is present.

3. If, on addition of a few drops of an 0.025 per cent. permanganate solution to the diluted blood, no methemoglobine appears within twenty minutes—if the blood remains clear and red, carbon monoxide-hemoglobine is present. The same quantity of permanganate added to an equally dilute solution of human blood or that of the ox, dog or rabbit, should give a yellow color, produce methemoglobine and render the solution turbid.

[1] Berichte d. deutsch. chem. Gesell. **13**, 1778. [2] Ibid. **13**, 1294.

4. Instead of the permanganate, a 1 per cent. solution of pyrocatechine or hydroquinone can be used, but they must be digested with the blood for 15 minutes at a temperature of 40°.

5. The spectra of hematine in acid solution and of methemoglobine can be easily distinguished only by the spectroscopic measurement of the position of the absorption bands.

By agitating 10 cc. of blood from five to seven times with six liter portions of the air to be tested, heating the blood to 90° or 95°, and passing a current of air through it, and then through an aqueous solution of palladium chloride, containing 1 part of the chloride to 50 of water, S. von Foder[1] is able to detect the presence of 0.5 of one volume of carbon monoxide in 10,000 of air. Metallic palladium is precipitated according to the following equation: $PdCl_2+CO+H_2O=CO_2+2HCl+Pd$.

By this method the author detected carbon monoxide in the blood of rabbits which had been kept for some time in an atmosphere containing only 0.4 of 1 part of the gas in the 10,000.

He recommends, also, the use of test papers prepared by moistening fine filter paper with a 0.2 per cent. solution of palladium chloride. A strip of the dried paper is suspended from a platinum wire in a 10 liter flask containing the air to be examined, and a little water. The flask is then closed. If the air contains $\frac{1}{2000}$ of carbonic oxide by volume, the paper becomes covered with a black film within a few minutes; if $\frac{1}{10000}$, after 2 to 4 hours; if $\frac{1}{20000}$, after 12 to 24 hours. It is however to be remembered that sulphide of hydrogen and ammonia will also blacken the papers.

To determine carbon monoxide quantitatively, a large volume of the air is passed through a series of absorption apparatus filled with a neutral solution of palladium chloride, the metallic palladium collected, dissolved in aqua regia, and subsequently determined by means of a standard solution of potassium iodide.

A. W. Hofmann[2] finds that triethylphosphine can be advantageously employed for the quantitative determination of carbon disulphide. A tubulated retort containing the compound is placed upon a water-bath, and connected with a cooler and receiver. The receiver is then connected with a series of three wide test tubes partially filled with caustic soda and a solution of triethylphosphine in ether. A current of dry carbon dioxide is passed through the apparatus and the retort heated. The operation is continued for several hours. The precipitate ($(C_2H_5)_3PCS_2$) is finally collected upon a weighed filter, dried in a vacuum and weighed. The method is especially adapted to the detection and determination of small quantities of carbon disulphide. By means of it the author found this compound in samples of mustard oil whose genuineness could not be questioned.

H. N. Morse.

[1]Dingler's polytechn. Jour. **237**, 456. [2]Berichte d. deutsch. chem. Gesell. **13**, 1732.

NOTES.

The Density of Iodine Vapor.

Victor Meyer concluded from Troost's experiments that the method of Dumas as well as his own for determining vapor densities gave the same results, and withdrew his suggestions to explain the possibility of disagreement. Crafts and Meier had suggested at the same time as V. Meyer that a diminution of tension due to the presence of air in the dissociable vapors, might cause a difference in the results of the two methods, and to this they still adhere. Troost afterwards established the variation of density with tension, and his conclusion was against the hypothesis of dissociation; to this CRAFTS and MEIER take exception. They have experimented with various methods and express their results graphically in the form of curves. These show that at a low temperature, 355° for example, the density of iodine vapor is normal, and has the same coefficient of expansion and of compressibility as air. For tensions of .1, .2, .3 and .4, the variation of density increases toward the middle of the curves, and becomes zero at high temperatures. Thus with low tensions also the density becomes constant between 1400° and 1520°, and equal to one-half the original. All facts accord with the hypothesis of gradual dissociation of the molecule I_2. This cannot be proved as in Deville's classical work, since the substance remains homogeneous; but the phenomena are such as would be observed if there were such dissociation, and this hypothesis offers the only explanation of the limit of diminution at one-half. The tendency of diminished tension to increase dissociation is well known.

The authors express the hope of being able to furnish a numerical basis for the speculation in the decomposition of the so-called elements founded on spectroscopic observations.—(*Comptes rendus, Jan.* 3, 1881.)

On Ozone.

HAUTEFEUILLE and CHAPPUIS have further studied, by means of the spectroscope, the formation and destruction of ozone with the following results: The absorption bands of ozone pure and dry, and formed from oxygen free from nitrogen, disappear slowly at ordinary temperatures, rapidly at red heat; and this takes place whether the ozone is enclosed in a vessel or is in the form of a gaseous current, the spectrum finally becoming continuous without the appearance of any new lines. The same phenomenon is observed in the destruction by heat of ozone mixed with nitrogen, the latter not having been exposed to electrical influence. There

is no indication of the formation of hyponitric acid. It is admitted that in ozonising oxygen in the presence of nitrogen at low electrical tensions, no hyponitric acid is formed. But the authors find that in ozonising at ordinary temperatures a mixture containing one-seventh nitrogen, there is always produced a new substance, indicated by remarkable absorption bands differing from those of electrified nitrogen, of nitrous, hyponitric and nitric acids. If the gas be passed through water the latter becomes acid, and the gas shows the spectrum of ozone only. So, too, if the gas be not dry, the new lines rapidly disappear. The same gaseous mixture is quickly destroyed at red heat, the bands of ozone and of the new substance disappearing, and those of hyponitric acid appearing and persisting. If the slow decomposition at ordinary temperatures be followed with the spectroscope, it is seen that the new bands disappear in from 24 to 48 hours before there is a trace of hyponitric acid. The latter then slowly appears; from which the authors conclude that the new substance decomposes into oxygen and nitric anhydride, and the latter into oxygen and hyponitric acid. Berthelot had observed that a mixture of hyponitric acid and oxygen subjected to electrical influence became colorless, and the authors in repeating the experiment find in the resulting mixture the new substance, but no hyponitric acid. They suggest the probable existence of a pernitric acid analogous to the persulphuric acid discovered by Berthelot.—(*Comptes rendus*, *Jan.* 10, 1881.)

On Nitrification.

Schönbein attributed the formation of nitrates to the union of ozone and nitrogen, but Berthelot has stated that this union does not take place directly. HAUTEFEUILLE and CHAPPUIS have shown, however, that it does take place under the influence of electricity of low tension with the production of a new substance, probably pernitric acid. The gaseous mixture was subjected to the influence of electricity of very low tension. The ozone was so diluted that it did not show absorption bands in a column two meters long, but there was a suspicion of bands of pernitric acid. When the current was heated with an alcohol lamp these appeared distinctly. The electrical tension was then increased as much as the apparatus would allow. The amount of pernitric acid formed increased progressively, but no hyponitric acid was obtained directly. The authors suppose that the formation of hyponitric acid, even at high tensions, may be due to the decomposition of pernitric acid by the greater heat of discharge.

Studying the effect of heat alone upon pernitric acid, they find that it is decomposed at all temperatures, but that at 130° the decomposition is completed in a few seconds, yielding oxygen and hyponitric acid. In order that the formation of pernitric acid should take place in the atmosphere, the presence of water vapor must be

no obstacle. The authors found, however, that the absorption bands of pernitric acid did not appear if the gas was not perfectly dry, but in this case liquid acid condensed upon the walls of the containing vessel. Thus by passing three liters of air with water vapor through the apparatus, they obtained .054 gram of nitric acid. From these experiments it is seen that nitric acid may be formed under varying conditions by the union of oxygen, or ozone, and nitrogen under the influence of electricity of low tension, pernitric and hyponitric acids being intermediate products.—(*Comptes rendus, Jan.* 17, 1881.)

Picene.

C. GRAEBE and J. WALTER have investigated more fully a hydrocarbon first obtained by O. Burg from the tar of brown coal, and called by him picene. The same compound is readily obtained when the residue from the rectification of California petroleum is subjected to dry distillation at a red heat. It is crystalline, and fuses at about 250°. It possesses a greenish yellow color, the lamellæ being often intensely green, the powder more yellowish. According to the analyses the substance has the formula $C_{21}H_{14}$ or $C_{22}H_{14}$. In perfectly pure condition it is colorless, and fuses at 330°–335°. It is possible that the crude material with which the authors worked is identical with which Morton worked some years ago. The hydrocarbon isolated by Morton and called thallene by him, is probably not quite pure picene, though from the published accounts of thallene it is impossible to decide this point. The boiling point of the substance was determined by the aid of the air thermometer constructed by Crafts, and was found to be 518–520°.—(*Ber. d. deutsch. chem. Gesell.* 14, 175.)

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AMERICAN CHEMICAL JOURNAL.

REVISION OF THE ATOMIC WEIGHT OF ALUMINUM.

By J. W. Mallet, F. R. S.,
Professor of Chemistry in the University of Virginia.

[*Continued from p.* 20.]

Second Series of Experiments.

Preparation and purification of Aluminum Bromide.—Aluminum bromide was prepared by the action of liquid bromine upon metallic aluminum of commerce, and was afterwards carefully purified. The first action is so violent that without special precaution the process involves some danger. In a first attempt a lump of aluminum weighing 15 to 20 grams was dropped into a long-necked flask containing a considerable quantity of bromine. There was little action for a few moments, but as soon as it began vivid combustion took place, torrents of bromine vapor were driven forth, and after the flask had cooled the surplus metal was found to have been completely fused and had nearly melted its way through the glass.

By the following arrangement the bromide was prepared in large quantity and without any trouble. About 50 cc. of bromine was placed in a large untubulated retort of hard Bohemian glass, the neck of the vessel standing vertically upwards, and an elongated

piece of ingot aluminum, the upper end of which was firmly tied with aluminum wire to a glass rod, was cautiously dipped into the liquid and withdrawn as soon as violent action began. By alternately lowering and raising the glass rod the lower end of the metal was immersed in the bromine at intervals short enough to keep up the temperature of the latter and make the action practically continuous, while there was no actual ignition, and but little bromine vapor was lost. As soon as a considerable portion of this bromine had become converted into aluminum bromide the further action became manageable. The remainder of the main quantity of metal to be treated was now at once added in lumps of 10 to 20 grams each; a long tube funnel with a glass stop-cock near the upper end was introduced into the neck of the retort, and liquid bromine was allowed to drip in at just such a rate as to keep up steady but not inconveniently violent action, taking care to keep the metal always covered. When the pieces of metal had nearly disappeared the supply of bromine was stopped, about 30 grams more of aluminum was added in filings, the contents of the retort were digested for 4 hours at about 230° C., and the fluid portion was then decanted off from the insoluble residue into another (tubulated) retort. Most of the silicon was left undissolved as a brown amorphous powder. Most of the iron was converted into ferric bromide, which, during the continued heating, was in part broken up, leaving ferrous bromide instead. A little copper derived from one sample only of the aluminum used, was of course converted into bromide also.

More than a kilogramme of crude aluminum bromide being thus prepared, it was purified by repeated fractional distillations at carefully regulated temperature, using as a receiver in each case the retort to be next employed, and adding each time, except the last, a few grams of aluminum filings. About a sixth of the whole amount was each time first distilled off and rejected as liable to contain silicon bromide, a little of this compound actually occurring in the earlier distillations; and another sixth was left behind, in order to retain the iron, which was separated with greater difficulty. After five distillations the bromide was obtained perfectly colorless, and boiling steadily at 263.3° C. under 747 mm. pressure. Specimens were dissolved in water, and carefully examined for iron, silicon, copper, and other conceivable impurities, but none could be found. As an additional precaution, the last distillation was

effected in a slow stream of pure nitrogen, so as to avoid any formation of oxide or oxybromide of aluminum, the propriety of this being suggested by Berthelot's recent results[1] as to the thermic relations of aluminum to oxygen and the haloids, and the distillate was collected in three successive portions, the results of whose analysis will be separately given further on; they go to show that these three portions were sensibly identical. The individual specimens of pure bromide required were collected in little tubes of thin, hard glass, previously closed in at one end, carefully dried, and sealed at the other as soon as the tube was nearly filled, the fused bromide having been introduced through a miniature tube funnel to avoid smearing the upper end of the collecting tube, and a new, perfectly dry funnel used each time. The weight of each collecting tube had been taken beforehand, and the piece of glass drawn off in sealing being washed, dried, and weighed, the weight of the sealed tube itself was known, the difference between this and the total weight of tube and contents giving the amount of bromide.

Experiments to determine the amount of bromine in this compound by precipitation with a silver solution have the advantage over those of Dumas, above quoted, upon the chloride that, as Stas has shown,[2] silver bromide practically does not share with the chloride of this metal the slight solubility in the exactly neutralized liquid from which precipitation has been effected which renders difficult an exact determination of the amount of silver needed. Pursuing in general the course so carefully examined by Stas, the following were the details of the method employed.

Preparation of pure metallic silver.—Pure metallic silver was prepared by dissolving in nitric acid nearly pure silver already on hand, diluting largely, precipitating with pure hydrochloric acid, digesting the precipitate with aqua regia, washing thoroughly, and reducing the purified chloride in the liquid way with sodium hydrate (from metallic sodium) and invert-sugar (from perfectly pure and well crystallized cane-sugar boiled with dilute hydrochloric acid). The metal, after having been carefully tested, was fused by a jet of purified hydrogen mixed with rather less oxygen than necessary for perfect combustion. To avoid the necessity for any cutting up afterwards with steel tools, the pulverulent metal was

[1] Bulletin de la Société Chimique de Paris, 20 Mars, 1879, 263.

[2] Comptes rendus, 73, 998. Annales de Chimie et de Physique [5], 3, 289.

divided into a number of little lots of various weight, and these were supported upon the surface of little blocks made by compressing pure sugar charcoal (from cane-sugar quite free from heavy metals) made into a paste with pure cane-sugar syrup and gradually drying and heating to redness.[1] The fused silver thus obtained was examined for occluded oxygen, following the method of Dumas[2] in his recent experiments. It was supported upon a thin layer of pure lime in a hard glass tube, and heated to moderate redness in a Sprengel vacuum. The amount of oxygen given off was less than that obtained by Dumas, doubtless owing to the fact that his silver was fused under nitre and borax, while mine was, as just stated, melted on a surface of carbon with no flux. He obtained at the rate of 57 cc. of oxygen (for 0° C. and 760 mm.) per kilogramme of silver, and in other experiments, prolonging notably the time of fusion, as much as 158 cc. and 174 cc. I obtained but 34.63 cc. per kilogramme, and in another experiment made by Mr. Santos, then a student in this Laboratory, the silver having been fused upon ordinary wood charcoal, but 30.12 cc. was given off. All the silver used in the atomic weight determinations was, in separate portions, heated in the Sprengel vacuum as long as any gas was expelled, and, having been treated with pure hydrochloric acid to remove any possibly adhering particles of lime, the granules were finally washed with pure water, dried, and kept for use in a glass stoppered bottle. An approximate calculation having been made of the quantity of silver which would be required to precipitate each of the specimens of aluminum bromide, an amount less than this by something under a decigramme was dissolved in nitric acid in a strong flask closed with a stopper, which was carefully opened when cold, and the contents were somewhat further diluted with water. The amount of specially purified nitric acid used was apportioned so as to leave the smallest possible excess after solution of the metal.

Precipitation of silver bromide.—Details of method used.—To avoid the danger of losing aluminum bromide when it was brought in contact with water, the action being quite violent and attended with dispersion of white fumes, each one of the sealed thin glass tubes containing the bromide was, when the time came for using

[1] This form of support had the advantage that if any particles of carbon should be mechanically enclosed in the silver they would be readily seen on solution of the latter in nitric acid.

[2] Comptes rendus, 86, 65. Chem. Centralblatt, 27 Febr. 1878, 138.

it, cautiously marked with transverse scratches at intervals of about half-an-inch by means of a writing diamond, and a strong glass bottle with a very well ground stopper having had a sufficient quantity of pure water placed at the bottom, the tube was broken across at the uppermost scratch, above the surface of the bromide, the empty point was dropped into the bottle, and the rest of the tube carefully lowered by means of a loose fitting spiral of platinum wire held sideways, so as to rest by the closed end on the bottom of the bottle without allowing the water to reach the bromide until the stopper had been inserted and tied down. By now gently inclining the bottle the water was brought very gradually into contact with the aluminum bromide, without dangerously violent action and without possibility of loss.

As soon as solution was complete and the bottle had cooled down the stopper was removed, any liquid adhering to it washed back into the bottle, and a stout glass rod with square end was used to gently crush the tube to small fragments, as otherwise its contents could not have been brought fairly into contact with the silver solution, since the interior of the tube would have become plugged up with silver bromide. The scratches previously made upon the glass rendered it easy to break it up without any splashing, and the rod was then well washed with pure water allowed to run directly into the bottle. The silver nitrate solution destined for this particular specimen was now washed out of the flask in which it had been shortly before prepared into the bottle containing the bromide, the stopper was again inserted, and the bottle was vigorously shaken as in the usual Gay-Lussac silver assay. The precipitation of the bromine was completed with a very carefully adjusted solution of silver nitrate, containing 1 milligramme of silver per cubic centimetre, and delivered from a burette[1] reading clearly to $\frac{1}{20}$th cc. The correspondence in capacity of the burette and measuring flask used was well ascertained. It was at first intended to use, for some at least of the experiments, *an excess* of silver, filter off the silver bromide formed, and determine silver in the filtrate by Volhard's method[2] with a standard solution of sulpho-cyanate; but this plan was abandoned as less simple, and probably requiring further investigation in regard to inherent

[1] This burette was simply drawn down to proper bore at the bottom, and the flow of the liquid was regulated by the admission of air through a well ground stop-cock at the top.

[2] Fresenius' Zeitschrift für analyt. Chemie, 18ter Jahrg., 2tes u. 3tes Heft., S. 271.

sources of error and limits of accuracy. The completion of the reaction was therefore ascertained simply by very cautious addition of the standard silver solution until all trace of turbidity ceased, verifying the result by counter test with a drop of very dilute solution of potassium bromide. By letting the bottle stand for a little while after each addition of silver solution and shaking, and then tilting it to one side so as to bring the upper portion of the liquid above the line it had before occupied on the glass, letting the new drop fall gently in, an exceedingly slight cloud was easily seen.

It should be added that the silver globules and the tubes of aluminum bromide, after final cleansing and drying, were handled only with forceps, so as to avoid any risk of traces of chlorides being taken up from the fingers, and due attention was given to the freedom of the laboratory atmosphere from hydrochloric acid or chlorine in other volatile forms.

Direct results of second series of experiments.—The results of the experiments made in this way were—

A.—Aluminum bromide from first portion of last distillate.

I.—	6.0024	grams of $AlBr_3$	required	7.2793	grams of Ag	for precipitation.
II.—	8.6492	"	"	10.4897	"	"
III.—	3.1808	"	"	3.8573	"	"

B.—Aluminum bromide from second portion of last distillate.

IV.—	6.9617	grams of $AlBr_3$	required	8.4429	grams of Ag	for precipitation.
V.	11.2041	"	"	13.5897	"	"
VI.—	3.7621	"	"	4.5624	"	"
VII.—	5.2842	"	"	6.4085	"	"
VIII.—	9.7338	"	"	11.8047	"	"

C.—Aluminum bromide from third portion of last distillate.

IX.—	9.3515	grams of $AlBr_3$	required	11.3424	grams of Ag	for precipitation.
X.—	4.4426	"	"	5.3877	"	"
XI.—	5.2750	"	"	6.3975	"	"

Third Series of Experiments.

Preparation of pure metallic aluminum.—A further supply of pure aluminum bromide having been made as above described, it was used to prepare metallic aluminum by reduction with sodium.

With a view to render the bromide more manageable while in contact with the air, it was decided to unite it with an alkaline chloride, as the aluminum and sodium chloride is used in the ordinary process of Deville, and in order to keep down the melting point, a mixture of both potassium and sodium chlorides was employed. The two alkaline salts were separately purified, carefully tested, well dried in platinum vessels, mixed in the proportion of one molecule of each, the mixture fused in lots of about 250 grams in a platinum dish over a gas furnace, poured out into another such dish standing on a block of cold iron, the thin cake gently crushed to a coarse powder while still warm in a mortar of hard glazed porcelain (from which, it was afterwards proved by examination, no silica was taken up), and the pulverized product kept until needed in a well stoppered bottle. Separate portions of the purified aluminum bromide having been in the last distillation collected in tared glass flasks and weighed, a quantity of the above mixture of alkaline chlorides was weighed off for each corresponding to 1 molecule $(K+Na)Cl$ for 1 molecule $AlBr_3$, and the flask having been heated until the bromide was fused, the potassio-sodic chloride was cautiously added. Very marked rise of temperature occurred, so that in a first attempt, using considerable quantities of the materials and mixing them abruptly, since such an effect had not been foreseen, the flask was violently cracked, and torrents of aluminum bromide vapor were driven off. This evolution of heat is interesting as evidence of chemical combination taking place, not only between two chlorides or two bromides, but between a chloride and a bromide. The fused mass was on cooling crushed to small fragments and coarse powder and preserved in a well-stoppered bottle. The precaution was not omitted of testing for any evidence of impurity derived from the flasks or mortar, but with negative result. The material thus prepared did not fume in the air, was sufficiently slow in taking up atmospheric moisture to be managed without difficulty, and fused on re-heating to about 130° C. The sodium to be used in decomposing it was in large ingots, which when needed were wiped to remove naphtha, the outer crust cut off with a knife, the large pieces roughly weighed, and the proper quantity rapidly cut up into small fragments without again moistening with naphtha.

The great difficulty in the way of obtaining pure metallic aluminum consists in obtaining crucibles of suitable material, especially

such as shall not yield either iron or silicon. M. Tissier[1] seems to have been more fortunate than I in the use of carbon vessels. The crucibles of hard carbon which I had on hand, purchased in Germany, contained both the above-named impurities, which were taken up in no small quantity by the aluminum; and I failed in sundry attempts to make crucibles of purer carbon, or to use this substance as a lining, the carbon either burning away, crumbling up, or permitting the fused materials to pass through its pores or through cracks in the mass. I at last succeeded in adapting to my purpose alumina itself, sufficiently cemented together by sodium aluminate. I was indebted to Henry Pemberton, Esq., Vice-President of the Pennsylvania Salt Manufacturing Company at Natrona, Pennsylvania, and to W. N. Richard, Esq., of the same works, for an abundant supply of aluminum hydrate, such as is thrown down by a stream of carbon dioxide from solution of sodium aluminate in the process of making soda from cryolite. This was not absolutely free from iron, but one lot contained traces only of this metal, insufficient, as it turned out, to contaminate the aluminum to be made in contact with it. The hydrate was strongly heated in well covered crucibles until it ceased to give off water; the alumina which was left required then to be guarded from the air, as it readily took up moisture again. All attempts to use it mixed with water and any unobjectionable cementing material to a plastic mass failed from excessive shrinkage and crumbling, but by mixing it in the dry state with dry sodium aluminate better results were obtained. The sodium aluminate had to be specially prepared, as that made (for soap-boilers' use) at Natrona from cryolite contained too much iron. The dry mixture was pressed into wooden moulds, and three or four crucibles thus made having been very slowly and cautiously heated up in a gas furnace, stood fairly the necessary temperature of the reduction of aluminum, although they were very fragile. On the whole, however, it was found best to use a highly aluminous Beaufaye crucible, with a thick lining of this mixture of dry alumina and sodium aluminate well rammed in and very gradually heated. There were some failures from cracking of the crucibles or linings, and whenever the slightest contact of the metallic aluminum with the outer crucible occurred, silicon and generally iron were sure to be found in the metal. With successful prevention of this by an adequately thick and perfectly continuous lining

[1] Comptes rendus, *loc. cit.*

there was much difficulty in securing a sufficiently high temperature in the interior, since the conducting power for heat of the alumina linings seemed to be quite low. This led to much loss of sodium by combustion, and but a very small yield indeed of really pure aluminum was secured. When the crucible had been heated up ready for the reduction, a small quantity of the pulverized mixture of potassium and sodium chlorides was thrown in; soon afterwards the aluminum bromide (which had been fused with the alkaline chlorides) with the proper quantity of sodium was introduced,[1] and as soon as the violent reaction was over a further portion of the mixed alkaline chlorides.

Only the large, well-fused globules of aluminum were picked out; these were re-fused once or twice before a blowpipe flame upon a support of alumina, to free them from any possible remains of the flux; any trace of oxide was detached by acting slightly upon the surface with pure hydrochloric acid, and the globules were then well washed with water, and dried by a gentle heat. Specimens cut from different portions of the globules were carefully tested, particularly for silicon, iron, sodium, and potassium; and a sufficient quantity of the metal for the intended experiments was found to yield no appreciable trace of impurity. The surface of the specimens to be used which had touched the cutting pliers was again cleansed by acid and water. This pure aluminum did not differ much in physical character from the ordinary metal of commerce: it seemed, however, to be somewhat whiter, was distinctly softer, and had a little higher density, the mean of three closely agreeing determinations made at 4° C. giving the number 2.583 as referred to water at the same temperature.

Production of hydrogen by aluminum, and measurement of the gas.—Details of method used.—The pure metal was used for the determination of its atomic weight by acting upon a known weight of it with a strong solution of sodium hydrate and determining the amount of hydrogen evolved. The advantage of using an alkali rather than hydrochloric acid, as in Terreil's experiment above quoted, lies in the non-volatility of the former, only vapor of water having to be separated from the hydrogen, while sulphuric acid is

[1] Aside from the question of expense there is some advantage in using aluminum bromide for making the metal, on account of the low melting-point of the sodium bromide which is left. Carnelley's recent determinations (Chem. Soc. Journ., July, 1878, pp. 279, 280) make the melting-point of sodium bromide 708° C., while that of the chloride is 772°, and that of the fluoride above 902°.

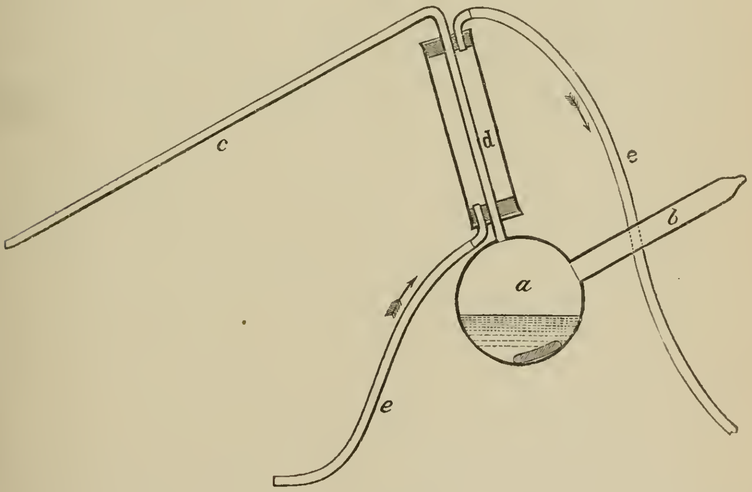
not available on account of the resistance to its action of aluminum. In 1863 Fr. Schultze [1] proposed to measure the volume of hydrogen given off by the action of an alkaline solution on commercial aluminum as the means of approximately deciding on the comparative purity of different specimens. The nature of the reaction was established by preliminary experiments, which proved to me that normal sodium aluminate alone is formed, so that each atom of aluminum liberates three atoms of hydrogen. The sodium hydrate was prepared from metallic sodium, and was used in the form of a solution so strong as scarcely to lose a sensible amount of water by the passage through it of a dry gas at common temperature—such an alkaline solution, so far as strength is concerned, as would be used to absorb carbon dioxide in an organic analysis. The quantity taken for each experiment was but a few cubic centimetres, and but little beyond the exact amount required for the solution of the metal; a small excess was, however, always allowed, so that the action might not become very languid towards the end. This strong alkaline solution was prepared with water which had been boiled to expel air, and the solubility in it of hydrogen was ascertained to be so small that any correction on this account would have fallen within the limits of inevitable error, and might be safely neglected.

To secure accurate measurement of a somewhat large volume of hydrogen, two stout flasks were selected, one holding about a litre and the other about half as much, and with narrow necks of rather more than usual length; and on the necks a simple millimetre scale was marked. One of these flasks having been carefully filled with mercury and inverted over the mercurial trough, the hydrogen was collected in it, such a quantity of aluminum being used in each experiment as previous trials had shown would yield gas enough to bring the level of the mercury within the range of the scale on the neck. To thus obtain such a volume of gas as could be accurately measured in the narrow part of the flask it was necessary to note in advance roughly the prevailing temperature and pressure, and to take advantage of a time when these were not undergoing much change. The level of the mercury having been noted on the millimetre scale, the corresponding volume was afterwards determined by calibration with mercury, weighed in portions of about half a kilogramme.

[1] Fr. Schulze, "Die gasvolumetrische Analyse," S. 18, quoted in v. Wagner, Jahresbericht, u. s. w., 1864, S. 23.

The little piece of apparatus used for the solution of the aluminum is shown in fig. 2, in which (*a*) represents a glass bulb of about 65 mm. diameter; (*b*) a tube connected therewith, originally open at both ends, and about 12 mm. diameter and 175 mm. long, but afterwards reduced in length to about 100 mm. by drawing off and sealing, as shown in the figure; (*c*) is the much smaller tube for carrying off the gas produced; (*d*) is a water jacket like that of the common Liebig's condenser, formed by a piece of larger tube surrounding the ascending limb of (*c*), and put in place before (*c*) was bent; while (*e*, *e*) represent small india-rubber tubes for circulating a current of water through (*d*).

Fig. 2



Each experiment was made as follows: The proper quantity of strong solution of sodium hydrate, its volume accurately measured, having been introduced into the bulb by means of a little tube funnel passed through (*b*), taking care to leave the surface of the latter clean, the aluminum (usually in a single piece of elongated shape) was passed into (*b*), held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 mm. from it. (*b*) was now drawn off and sealed with a well-rounded end. The bulb was touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube (*c*) was introduced into the mercury of the trough, taking care that

(*b*) was still kept in such a position as to prevent the aluminum coming in contact with the alkaline solution. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in (*c*) were read off[1]; so that, knowing the volume of alkaline solution introduced and of aluminum (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to determine the volume of air which the apparatus contained at the beginning. The aluminum was now made to slide down into the bulb, the end of the gas-delivery tube (*c*) having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of aluminum rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water; while, on the other hand, it sometimes became necessary to gently warm the liquid towards the end of the experiment. To guard against more than traces of aqueous vapor being carried away with the hydrogen, a current of ice-water was kept up through (*d*). As soon as the last of the aluminum had disappeared, leaving the liquid quite clear, (*c*) was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer, height of mercury in (*c*) above that in trough, and level of mercury in neck of measuring flask (after the last traces of moisture had been removed from the hydrogen by means of a stick of caustic potash), with its height above that in trough, were now read and recorded. Lifting (*c*) straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in (*a*), (*b*), and (*c*) was filled up with alkaline lye of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube funnel, and the volume used noted, so as to show how much liquid had been already present. The apparatus being now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference between the total capacity (to the level of the

[1] All readings were of course made from a distance with the aid of a small telescope.

mercury in (c)) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the volume of gas collected in the flask.

In order to connect the weight of the aluminum with the weight of the hydrogen, the latter being obtained from its observed volume and Regnault's determination of its density, it was necessary that the weight of the metal should be absolute, or in terms of equal value with those used in Regnault's researches; hence, as has been already stated, the weights used were such as had had their real value determined, and the precaution of double weighing was applied. The quantities of metal used being small, the centre of gravity of the balance beam was so adjusted as to give great sensitiveness.

In calculating the weight of the hydrogen from its volume, the difference in the value of the force of gravity at Paris and at the University of Virginia had to be taken into account. In view of the difference of latitude and elevation above the sea this constant is, in C.G.S. units,

For Paris	980.94
For University of Virginia . .	979.95

and, applying the difference in nominally normal pressure at the two places, Regnault's value for the weight of a litre of hydrogen at 0° C. and 760 mm., .089578 gram, becomes .089488 gram.

In the experiments made in this way the only assignable cause of constant error, tending to affect in a particular direction the atomic weight deduced from them, seems to be the retention in solution of traces of hydrogen by the alkaline liquid in the bulb. The tendency of this is, of course, to make the atomic weight of aluminum appear greater than it should be, but I am satisfied that the possible extent of such error must be excessively minute, inappreciable within the limits of error of observation.

Direct results of first set of third series of experiments.—The results obtained were as follows:—

A.—Hydrogen by volume at 0° C. and 760 mm.

I.—.3697	gram of	Al gave	458.8	cc.	=.04106	gram of H.
II.—.3769	"	"	467.9	"	=.04187	"
III.—.3620	"	"	449.1	"	=.04019	"
IV.—.7579	"	"	941.5	"	=.08425	"
V.—.7314	"	"	907.9	"	=.08125	"
VI.—.7541	"	"	936.4	"	=.08380	"

Second set of experiments of third series.—Hydrogen collected and weighed as water.—Details of method used.—As the collection and accurate measurement of larger quantities of hydrogen would be difficult from the great weight of mercury to be dealt with, while it seemed desirable to repeat these experiments with a larger amount of aluminum, an arrangement was adopted for burning the hydrogen and weighing it as water.

A bulb like that described above was used for the reaction between the aluminum and solution of sodium hydrate, another small tube (which may be designated as (x)) being connected, however, with the bulb, for the purpose of sweeping out air at the beginning of the combustion and the remainder of the hydrogen at the end by a current of other gas. The gas from the delivery tube (c) was carried through a series of four drying tubes, containing in the former two pumice stone soaked with pure sulphuric acid of full strength, and in the other two well dried asbestos and loose, woolly phosphorus pentoxide; thence it passed through a long combustion tube, filled for the first two-fifths with pure, finely granular cupric oxide, which had been recently ignited, and for two-fifths more with turnings of electrotype copper oxidized on the surface, while the last one-fifth of its length remained at first unoccupied, to be filled later as will be described; the vapor of water being finally collected beyond this combustion tube in a single light drying tube of calcium chloride, one of sulphuric acid on pumice, and one of phosphorus pentoxide.

The whole of the apparatus having been put together, with the exception of the three final drying tubes, for which at first a single unweighed calcium chloride tube was substituted, with sodium hydrate solution in the bulb, and metallic aluminum in the tube (b),

a slow stream of carefully purified and well dried air was passed through from (x) for some time, while the combustion tube was heated to low redness. Having allowed it to cool down to the temperature of the room, the stream of air from (x) was replaced by one of dry nitrogen; a plug of soft copper turnings with bright unoxidized surface was introduced into the further end of the combustion tube so as to fill up the unoccupied fifth of its length, and it was again brought to and kept at a red heat. After the nitrogen had passed through at this temperature for about twenty minutes, the three drying tubes for the collection of the water to be formed, having been standing for some time in the balance case, were accurately weighed, and connected with the further end of the combustion tube, the previously used and unweighed calcium chloride tube being removed. The tube (x) having been closed, the tube (b) was now tilted so as to make the aluminum slip down into the alkaline liquid, and as in the experiments already described, the rate at which the hydrogen was evolved was controlled by inclining the bulb so as to vary the extent of surface of the metal attacked, and by cooling the outside of the bulb with water.

As soon as the metal was all dissolved, nitrogen was again introduced by (x) to sweep out the remaining hydrogen, limiting the quantity of the former gas to such an amount as was thought necessary for this purpose. This nitrogen was then in turn replaced by pure and dry air, which was passed through the apparatus until the surface of the copper which had been reduced was reoxidized, this being done to avoid any risk of occluded hydrogen being retained, while the nitrogen had served to obviate the danger of explosion. The drying tubes were then finally removed from the further end of the combustion tube, and weighed after exposure to the atmosphere of the balance case long enough to permit the surface of the glass attaining a constant condition. In both weighings the reduction to equivalent weights *in vacuo* was duly attended to, the weights and densities of all the materials making up the drying tubes and their contents having been previously ascertained. The last tube of the set was weighed separately, as was the last of the drying tubes connected with the reaction bulb, and it was found that, there being no increase of weight on the part of either of them, the absorption of aqueous vapor was sensibly complete.

Although all the precautions I could think of were taken in these experiments, the well known difficulty of absolutely excluding moisture, of which every joint to the apparatus becomes a possible source, so that in ordinary organic analysis the amount of hydrogen found may be expected to come out rather above than below the truth, leads to the suspicion that such constant error as may have been involved tended in this direction, and if so that the resulting atomic weight would be made to appear somewhat too low. The extent of error from this cause, however, if it existed at all, must have been extremely small.

Direct results of second set of experiments of third series. The results of these last experiments were—

B.—Hydrogen weighed as water.

I.—2.1704	grams	of Al	gave	2.1661	grams	of H_2O.
II.—2.9355	"	"		2.9292	"	"
III.—5.2632	"	"		5.2562	"	"

Calculation of results.

In calculating the atomic weight of aluminum from the data furnished by the above described experiments, the atomic weights assumed for the other elements involved are those which result from the researches of Stas and the previous investigation by Dumas and Stas of the composition of water, namely—

$$O=15.961 \qquad S=31.996 \qquad N=14.010$$

In regard to silver and bromine a difficulty arises from the fact that the relation between these elements was determined by Stas with metallic silver which, as Dumas[1] has pointed out, contained in all probability occluded oxygen. It appears from Dumas' experiments and from mine, that the quantity of oxygen which may be so retained varies with the conditions under which the metal is fused, and it is impossible now to ascertain precisely how much was present in that used by Stas, while the correction to be applied on this account, though small, is not inappreciable in its effect upon the atomic weight of the aluminum. Omitting to extract in the Sprengel vacuum the occluded oxygen from the silver used in my

[1] *Loc. cit.*

experiments would not have secured identical condition of the silver with that of the metal used by Stas, since the circumstances of fusion and cooling would probably not have been altogether the same, and it seemed best to use silver fully purified in this respect, so that my results might be directly comparable with any obtained in the future, since this source of error once pointed out ought not to be hereafter neglected. I have therefore used as the atomic weights of silver and bromine the numbers obtained by Stas (from his experiments on silver bromide and bromate), recalculated on the assumption that the metal employed by him would have yielded 57 cc. (reduced to 0° C., and 760 mm.) or 82 mgrm. of oxygen per kilogramme, this being the quantity obtained by Dumas from silver treated as nearly as possible as was in all likelihood that which Stas employed. This has the advantage of reducing the remaining error to that only which depends on the *difference* between the real amount of oxygen which was present and that assumed in such calculation, instead of leaving the whole resulting from using Stas' numbers uncorrected, my silver having had the oxygen removed, while his had not been so treated. The atomic weights adopted then for these two elements are—

$$Ag=107.649 \qquad Br=79.754$$

Calculated results.—The following are the values obtained for the atomic weight of aluminum from the different series of experiments, with the probable (mean) value resulting from each set, the difference from this mean of each individual experiment, and the probable error of the mean itself calculated in the usual way by the method of least squares:

First series.

A. Experiment.		A. Diff. from mean.	B. Experiment.		B. Diff. from mean.
I.	Al=27.029	—.011	VI.	Al=27.114	+.018
II.	" 27.043	+.003	VII.	" 27.095	—.001
III.	" 27.055	+.015	VIII.	" 27.107	+.011
IV.	" 27.068	+.028	IX.	" 27.067	—.029
V.	" 27.005	—.035	X.	" 27.096	.000
Mean	" 27.040		Mean	" 27.096	
Probable error of mean result		±.0073	Probable error of mean result		±.0054

Second series.

A.

Experiment.		Diff. from mean.
I.	Al=27.035	+.001
II.	" 27.021	—.013
III.	" 27.046	+.012
Mean	" 27.034	

Probable error of mean result $\pm$.0049

B.

Experiment.		Diff. from mean.
IV.	Al=27.028	+.005
V.	" 26.993	—.030
VI.	" 27.036	+.013
VII.	" 27.028	+.005
VIII.	" 27.030	+.007
Mean	" 27.023	

Probable error of mean result $\pm$.0052

C.

Experiment.		Diff. from mean.
IX.	Al=26.999	—.019
X.	" 27.034	+.016
XI.	" 27.021	+.003
Mean	" 27.018	

Probable error of mean result $\pm$.0069.

Third series.

A.

Experiment.		Diff. from mean.
I.	Al=27.012	+.007
II.	" 27.005	.000
III.	" 27.022	+.017
IV.	" 26.988	—.017
V.	" 27 006	+.001
VI.	" 26.996	—.009
Mean	" 27.005	

Probable error of mean result $\pm$.0033

B.

Experiment.		Diff. from mean.
VII.	Al=26.995	+.005
VIII.	" 26.999	+.009
IX.	" 26.977	—.013
Mean	" 26.990	

Probable error of mean result $\pm$.0046

In view of the gradual loss of water which, as has been shown, crystallized ammonium alum undergoes on exposure to the atmosphere, I feel that of these various sets of experiments, B of the first series is entitled to least confidence, and the considerable difference between its results and the others leads me to favor its rejection. On the other hand, I am inclined to attach most weight to series 3, A, since the method used was very simple in principle, the determination of one of the two quantities concerned was

rendered very exact by the great volume occupied by the hydrogen, the comparison was made directly with the standard element in our system of atomic weights and not through the intervention of any other substance whose atomic weight must be assumed, and the agreement of the results among themselves is particularly good, as shown by the probable error of the mean being the smallest reached.

General mean of results.—The general mean from all of the thirty experiments, if all be included in the calculation, is $Al = 27.032$, with a probable error for this mean of $\pm .0045$.

If series 1, B, be excluded, the mean of all the remaining twenty-five experiments is $Al = 27.019$, with a probable error of $\pm .0030$. The third decimal having no positive value, we may take $Al = 27.02$. If integer numbers be used for O, N, C, Na, &c., $Al = 27$.

All the experiments which I have made are reported, except three or four in which there was manifest failure, as by accidental loss of material to a visible extent, and which were on that account not completed.

The general result adds, I trust, aluminum to the, unfortunately still limited, list of those elementary substances whose atomic weights have been determined within the limits of precision attainable with our present means of experiment.

Bearing of final result upon "PROUT'S *law*."

It is interesting to observe that this result also adds one to the cases already on record of the numbers representing carefully determined atomic weights approaching closely to integers, and leads to a word on the reconsideration of "Prout's law." The recent researches of Mr. Lockyer, not unsupported by evidence drawn from other sources, have tended to suggest the possibility, at least, that the forms of matter which as known to us under ordinary conditions we call elements may be susceptible of progressive dissociation at enormously high temperature, and, under circumstances in which this supposed state of dissociation admits of being spectroscopically observed, some of the characteristic features in the spectrum of what is usually known to us as hydrogen become in a very remarkable degree prominent. If such dissociation may really occur, and if the atoms of hydrogen as commonly

known to us form either the last term, or any term not far removed in simplicity from the last, in the progressive breaking up of other forms of matter, it is obvious that "Prout's law," or some modification of it, such as was many years ago suggested by Dumas, *must* be true, the atomic weights of all the other so-called elements must be multiples of that of hydrogen, or multiples of that fraction of the hydrogen atom which may result from the dissociation of this body itself. If such fraction be very small as compared with the effect of the inevitable errors of experiment, the experimental verification or refutation of the law will prove impossible, but if it be considerable, as for instance one-half of the commonly known hydrogen atom, or one-fourth, as assumed by Dumas, the question admits of practical examination.

Well deserved attention has for some years past been given to the labors of Stas in this direction, and his main result is no doubt properly accepted, if stated thus, that the differences between the individual determinations of each of sundry atomic weights which have been most carefully examined are distinctly less than their difference, or the difference of their mean, from the integer (or one-half or one-fourth unit) which Prout's law would require.

But the inference which Stas himself seems disposed to draw, and which is very commonly taken as the proper conclusion from his results, namely, that Prout's law is disproved, or is not supported by the facts, appears much more open to dispute.

It must be remembered that the most careful work which has been done by Stas and others only proves by the close agreement of the results that *fortuitous* errors have been reduced within narrow limits. It does not prove that all sources of *constant* error have been avoided, and indeed this never can be absolutely proved, as we never can be sure that our knowledge of the substances we are dealing with is complete. Dumas' late observations on the occlusion of oxygen by metallic silver constitute an illustration of this, some of the best of Stas' results being thereby undeniably vitiated, though probably to but a minute extent.

Of course one distinct exception to the assumed law would disprove it, if that exception were itself fully proved, but this is not the case.

As suggested by Marignac and Dumas, any one who will impartially look at the facts can hardly escape the feeling that there must be some reason for the frequent recurrence of atomic weights dif-

fering by so little from accordance with the numbers required by the supposed law.

As the question stands at present, the following 18 atomic weights are the only ones which may be fairly considered as determined with the greatest attainable precision, or a very near approach thereto, and without dispute as to the methods employed:

*Oxygen	15.961
*Nitrogen	14.010
Chlorine	35.371†
Bromine	79.757†
Iodine	126.541†
*Sulphur	31.996†
*Potassium	39.042
*Sodium	22.987
*Lithium	7.005
Silver	107.667†
Thallium	203.655‡
*Aluminum	27.019
*Carbon	11.97
*Phosphorus	30.96
Barium	136.84
Calcium	39.90
*Magnesium	23.94
Lead	206.40

If now we discard altogether Dumas' assumption of multiples of .5 or .25, and consider simply the indications afforded of Prout's law in its original form, we may safely take the first decimal place of each of these numbers as quite freed from the influence of *fortuitous* errors, while the second decimal is nearly so in many instances. It appears that out of the 18 numbers, 10 (those to which an asterisk is prefixed) approximate to integers within a range of variation less than one-tenth of a unit. What then is the degree of probability that this is purely accidental, as those hold who carry to the extreme the conclusions of Berzelius and Stas? Since there are five intervals of .1 each between any integer and the .5 which

† Stas' numbers, uncorrected for occlusion of oxygen by silver.

‡ Crookes' number modified by taking O=15.961 instead of 15.96.

divides it from the next higher (or lower) integer, the result is given by the expression—

$$5^{-18}\left\{1+\frac{18!}{17!}\times4+\frac{18!}{16!\,2!}\times4^2+\frac{18!}{15!\,3!}\times4^3+\ldots\frac{18!}{10!\,8!}\times4^8\right\}$$

and the probability in question is found to be only equal to 1 : 1097.8.

Of course this result might be easily varied by assuming other limits of precision as marking accordance with the law within the range of possible constant error, but this example seems to be based upon not unfairly assumed ground in this respect, and seems sufficiently to illustrate the point that not only is Prout's law not as yet absolutely overturned, but that a heavy and apparently increasing weight of probability in its favor, or in favor of some modification of it, exists and demands consideration.

Contributions from the Chemical Laboratory of Harvard College.

X.—ON FURFUROL AND CERTAIN OF ITS DERIVATIVES.

By Henry B. Hill.

[*Continued from p.* 51.]

Dibrommaleic Acid of Kekulé.

In 1864 Kekulé[1] found among the products of the action of bromine and water upon succinic acid an acid, $C_4H_2Br_2O_4$, to which he gave the name dibrommaleic acid. It formed white, clustered needles, which were extremely soluble in water, alcohol, or ether, and melted at 112°; at higher temperatures the acid distilled apparently unchanged, and it volatilized readily with steam. For the further characterization of the acid, Kekulé made the silver

[1] Ann. Chem. u. Pharm. **130**, 1.

and lead salts. The silver salt could be precipitated from an aqueous solution of the acid, by the addition of argentic nitrate; and, according to the concentration of the solution, it appeared as a granular, crystalline precipitate, or in slender, glistening needles. The dry salt exploded violently by heat or percussion. The lead salt was thrown down by the addition of plumbic acetate to an aqueous solution of the acid, and when air-dried it was found to contain a molecule of water.

Since its discovery by Kekulé, the acid prepared in this way has been mentioned but twice, as far as I know; and these notices contain no additional facts which could serve to assist in its identification. Bourgoin[1] gives its melting point as 110°, and asserts that it distils unaltered. Fittig and Petri,[2] in their attempts to prepare the tribromsuccinic acid, which had been described by Bourgoin, obtained dibromsuccinic acid and a substance crystallizing in hemispherical aggregations, which, from their melting point (112°) and volatility with steam, they recognized as dibrommaleic acid.

In 1873, Limpricht and Delbrück[3] described an acid of the same composition, which they made by the action of bromine and water upon mucobromic acid. They found it difficult of purification; and, in their study of it, they were to all appearance hampered by lack of material. The acid melted at 108–120°, and by sublimation it was converted into its anhydride, $C_4Br_2O_3$, which melted at 95–120°. The barium salt they obtained in colorless, tabular crystals, to which they assigned the formula, $BaC_4Br_2O_4 . 2H_2O$. The silver salt they found to be insoluble; but it did not explode either by heat or percussion. They assumed, apparently without hesitation, that this acid was isomeric with that of Kekulé, and therefore named it dibromfumaric acid.

The acid made by the action of bromine upon mucobromic acid, which I have just described, agreed in most respects closely with the acid described by Kekulé; and yet the higher melting point and the ready formation of the anhydride rendered a further comparison necessary in order to settle the question of identity.

In the preparation of dibrommaleic acid, I followed in general the method of Kekulé; but, since this was to be the main product of the reaction, I was obliged to use a greater proportion of bromine and water, in order to get any considerable yield.

[1] Bul. Soc. Chim. [2] **21**, 404; **22**, 443. [2] Ann. Chem. u. Pharm. **195**, 76.
[3] Ann. Chem. u. Pharm. **165**, 294.

I obtained good results by using to one part of succinic acid two of water and four of bromine, and heating twenty hours at 140°. The mother liquors from which the greater part of the dibromsuccinic acid had been separated were distilled, the distillate neutralized with baric carbonate, and the baric dibrommaleate precipitated from the filtered solution. After several precipitations from aqueous solution by alcohol, it was crystallized from water by evaporation, and dried by exposure to the air. The salt could not be distinguished in outward appearance from that made from mucobromic acid.

I. 2.4931 grams of air-dried salt lost in weight, at 125–130°, 0.2136 gram. 0.7670 gram of this dried salt gave, on ignition with H_2SO_4, 0.4393 gram $BaSO_4$.

II. 0.5899 gram air-dried salt gave 0.3102 gram $BaSO_4$.

Calculated for $C_4Br_2O_4Ba.2H_2O$.		Found. I.	Found. II.
Ba	30.78	30.79	30.91
H_2O	8.09	8.15	

The solubility of this salt was determined according to the method of V. Meyer.

8.9841 grams of a solution saturated at 20° gave 0.2912 gram $BaSO_4$.

The aqueous solution saturated at 20°, therefore, contains 5.71 per cent. of the anhydrous salt.

From this barium salt, the free acid was made in the manner above described. In its behavior towards solvents, it resembled perfectly the acid made from mucobromic acid, and it melted between 120° and 123°. This acid I did not analyze; but the analyses published by Kekulé show too high a percentage of bromine, and in this respect do not differ essentially from those I have given above.

Calculated for $C_4H_2Br_2O_4$.		Found by Kekulé. I.	Found by Kekulé. II.
Br	58.38	58.98	59.08

By heating this acid in a stream of carbonic dioxide, the anhydride could readily be made in appearance and behavior perfectly identical with the compound already described, and melting at 114°–115°.

I. 0.4160 gram substance gave 0.2860 gram CO_2 and 0.0032 gram H_2O.

II. 0.2840 gram substance gave 0.4165 gram AgBr.

Calculated for $C_4Br_2O_3$.		Found. I.	II.
C	18.75	18.75	
H	...	0.10	
Br	62.50		62.34

The identity of the dibrommaleic acids made by the action of dry bromine upon mucobromic acid and aqueous bromine upon succinic is thus sufficiently established. They each give an anhydride melting at 114–115°; their barium salts have the same composition, $BaC_4Br_2O_4.2H_2O$; and the solubility of these two salts in water is the same, the saturated aqueous solution containing in one case 5.66 per cent. of the anhydrous salt at 19°, in the other 5.71 per cent. at 20°.

Although I have several times tried the action of bromine and water upon mucobromic acid, according to the method of Limpricht and Delbrück, I have not as yet submitted the product obtained in this way to any very extended investigation. In all qualitative reactions it is identical with the acid I have described; and, considering the mode of its formation, one can hardly doubt its identity. Moreover, with regard to the slight differences which would seem to have induced Limpricht and Delbrück to consider their acid isomeric with Kekulé's, I have been unable to confirm their observations. The melting point (95–120°) given by them for the anhydride does not give confidence in the purity of their material. The higher percentage of barium (31.9)[1] which they found in their barium salt would be in no way at variance with my results, even if its purity were granted, since the material they analyzed had been dried *in vacuo* (over sulphuric acid ?), and my own experiments have shown that it slowly effloresces under these conditions.

Although the foregoing facts seemed to warrant the conclusion that the dibrommaleic acid of Kekulé belonged to the maleic series, inasmuch as the anhydride was the direct product of the reaction of bromine upon mucobromic acid, still I thought it advisable to

[1] Limpricht and Delbrück erroneously calculated the percentage of barium in the salt $BaC_4Br_2O_4.2H_2O$ as 31.9 per cent. instead of 30.78, and therefore gave the same formula.

prove this directly, more especially since all analogy pointed to the formation of a derivative of fumaric acid under the conditions essential to its preparation from succinic acid. I therefore dissolved in water the pure anhydride prepared from succinic acid, neutralized the solution with baric carbonate, precipitated the barium salt by alcohol, and recrystallized it from water. This salt proved to be identical with that which was obtained directly from the acid.

0.7525 gram of the air-dried salt lost on heating to about 120° 0.0581 gram; 0.6933 gram of this dried salt gave 0.3922 gram $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found.
Ba	30.78	30.69
H_2O	8.09	7.72

The solubility was also determined by the method of V. Meyer.

7.6833 grams of the solution saturated at 19.5° gave, on evaporation with H_2SO_4 and ignition, 0.2446 gram $BaSO_4$.

An aqueous solution saturated at 19.5° contained therefore 5.58 per cent. of the anhydrous salt.

This proves that dibrommaleic acid may be carried unchanged through its anhydride, and that it consequently belongs to the maleic series, unless, indeed, its behavior is radically changed by the complete replacement of its hydrogen by bromine. That such is not the case has recently been shown by Bandrowski,[1] who has discovered an acid of the same composition, which is undoubtedly dibromfumaric acid. This acid melts at 219–220°, and by distillation is converted into dibrommaleic acid.

Mucobromic Acid with Oxidizing Agents.

The close connection between mucobromic acid and dibrommaleic, as shown by its behavior when heated with bromine, naturally suggested the direct conversion of the one into the other by oxidation.

An aqueous solution of chromic acid does not act upon mucobromic acid at ordinary temperatures, even after standing for weeks. On warming, carbonic acid is freely given off, and at the same time a sharp, acroleïn-like odor is noticed. If one atom of oxygen is employed for every molecule of mucobromic acid, a portion of the mucobromic acid seems to be completely destroyed, while nearly one-half of it remains unaltered, and may be extracted

[1] Berichte der deutsch. chem. Gesellsch. 12, 2213.

with ether after the reaction is completed. When two atoms of oxygen are taken, but little mucobromic acid escapes oxidation; but I have been unable to isolate well-marked products of the reaction, in any considerable quantities. When the solution is distilled, the substance possessing the sharp, pungent odor passes over with the steam. It is quite soluble in water, although not in all proportions, and its aqueous solution reduces silver energetically from the oxide even in the cold. Although this is the most striking product of the oxidation, it is formed in such small quantities that I have as yet been unable to study it further. After this volatile product has been distilled off, but a trace of organic acid can be extracted from the retort residue by ether. This acid is chiefly mucobromic; but with it I have found dibrommaleic acid in quantity barely sufficient for the recognition of its barium salt under the microscope when precipitated from aqueous solution by alcohol. The oxidation with nitric acid gives somewhat better results. When mucobromic acid is boiled with ten times its weight of nitric acid of sp. gr. 1.20, carbonic dioxide is slowly given off, the escaping gas renders a solution of argentic nitrate turbid, and yet, if the heat is continued for several hours, a considerable portion of the mucobromic acid is found to be converted into dibrommaleic acid. In one experiment I obtained, after several hours' boiling, from 5 grams of mucobromic acid 2.3 grams of baric dibrommaleate and 1.5 gram of unaltered mucobromic acid. This corresponds to nearly forty per cent. of the theoretical yield of dibrommaleic acid from the mucobromic acid which entered into the reaction. Stronger nitric acid oxidizes more rapidly, but the yield of dibrommaleic acid is smaller; if much more dilute acid is used, the mucobromic acid is hardly altered.

Precisely the same effect is produced by long boiling with bromine water, carbonic dioxide being evolved as before, and the yield of dibrommaleic acid remaining essentially the same. The identity of the acid made by bromine water was established by the analysis of the barium salt. This salt was precipitated several times from aqueous solution by alcohol, recrystallized from water, and contained then the required percentage of barium.

0.5493 gram of the air-dried salt gave 0.2887 gram $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found.
Ba	30.78	30.90

Limpricht found that mucobromic acid was the only product when pyromucic acid suspended in water was treated with an excess of bromine at ordinary pressures. Since mucobromic acid is itself converted into dibrommaleic acid by boiling it with bromine water, it follows that the latter acid must of necessity be formed in the preparation of mucobromic acid. For its detection, the mother liquors, from which the mucobromic acid had been separated as completely as possible, were distilled. The distillate, consisting chiefly of concentrated hydrobromic acid (b. pt. 126°) was partially neutralized with potassic carbonate, and thoroughly shaken out with ether. The residue left on the evaporation of the ether was taken up with water, and the acid solution saturated with baric carbonate. Alcohol precipitated from the filtered solution baric dibrommaleate in characteristic form. For analysis, the salt was recrystallized from water, and dried by exposure to the air.

0.4709 gram of this salt gave 0.2516 gram $BaSO_4$.

Calculated for $BaC_4Br_2O_4.2H_2O$.		Found.
Ba	30.78	31.41

Since the percentage of barium was found to be too high for further identification the acid was set free, and converted into the anhydride by sublimation. This crystallized in the characteristic flattened needles, which melted at 114°. The quantity of dibrommaleic acid formed in the ordinary preparation of mucobromic acid is very inconsiderable, and amounted in one case to about one per cent. of the pyromucic acid employed. The quantity must, however, of necessity be very variable.

The oxidation of mucobromic acid by means of argentic oxide was investigated by Schmelz and Beilstein. They gave to the chief product of the reaction the formula $Ag_3C_7H_2Br_3O_5$; but it is evident from an inspection of their analyses that they had in their hands the silver salt of dibrommaleic acid in a nearly pure condition.

	Calculated for $Ag_3C_7H_2Br_3O_5$.	Calculated for $Ag_2C_4Br_2O_4$.	Found by Schmelz and Beilstein. I.	II.	III.	IV.	V.	VI.
C	11.51	9.84	10.07	10.64	11.30	...	...	...
H	0.27	...	0.64	0.37	0.32	...	...	...
Br	32.87	32.78	...	...	...	32.47	...	...
Ag	44.38	44.27	...	...	...	...	44.25	44.26

With this close agreement between the observed and calculated percentages, I did not consider it worth while to analyze, myself, this silver salt. Still it was evidently necessary to prepare from it the barium salt in order to compare this with the product I had already studied.

Since argentic bromide is readily formed when the silver salt of mucobromic acid is heated with water, I added at once an excess of argentic oxide to a warm solution of mucobromic acid, and heated it quickly to the boiling point. The oxidation seemed to be more neatly accomplished in this way than by the gradual addition of the argentic oxide, although even then there was formed a considerable quantity of argentic bromide. After the action had ceased, the whole was acidified with hydrochloric acid, and the filtered solution shaken out with ether. The acid left upon evaporation of the ether was then taken up with water, neutralized with baric carbonate, and the barium salt purified as before. An analysis of the air-dried salt, and a determination of its solubility, proved that the acid was identical with that made by the action of bromine upon succinic or mucobromic acid.

0.5225 gram of the air-dried salt gave 0.2741 gram $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found.
Ba	30.78	30.84

9.2092 grams of an aqueous solution saturated at 18.5° according to the method of V. Meyer, gave on evaporation with H_2SO_4 and ignition 0.2944 gram $BaSO_4$.

According to this determination, an aqueous solution saturated at 18.5° contains 5.61 per cent. of the anhydrous salt.

This oxidation of mucobromic acid by means of argentic oxide into dibrommaleic acid,

$$C_4H_2Br_2O_3+O=C_4H_2Br_2O_4,$$

would seem to show conclusively that it is the half aldehyde of the dibasic dibrommaleic acid.

Decomposition by Heat.

If mucobromic acid is quickly heated, the greater part of it distils unchanged; but, if the temperature is so regulated that it can distil but slowly, a great part of it suffers decomposition. The

reaction which it undergoes I have, as yet, studied only so far as to prove that dibrommaleic acid is one of the chief products. If the acid is mixed with sand and slowly distilled, streams of hydrobromic acid and carbonic dioxide are given off, and a colorless oil passes over, which, on standing, partially solidifies. On the addition of water, the solid portion dissolves, leaving an oil which is volatile with steam, and is not wholly soluble in water. Its aqueous solution reduces argentic oxide, and possesses an intolerably sharp, pungent odor. In the investigation of this oil, I have not yet obtained definite results.

The aqueous solution contained dibrommaleic acid, which was identified by an analysis of its barium salt. The solution of the barium salt obtained, at first was highly colored, and from it pure material could be made only by repeated precipitation from aqueous solution with the smallest possible quantity of alcohol. In this way, a perfectly colorless salt was made, and it was then recrystallized from water.

0.6652 gram of the air-dried salt gave 0.3498 gram $BaSO_4$.

Calculated for $BaC_4Br_2O_4.2H_2O$.		Found.
Ba	30.78	30.91

The amount of dibrommaleic acid thus formed is about 15 per cent. of the mucobromic acid taken, and 30 per cent. of the total weight of the distillate.

Action of Baric Hydrate.

The action of baric hydrate upon mucobromic acid was first studied by Schmelz and Beilstein. The results they obtained were extremely interesting, but needed extension in several directions. More especially inviting was the muconic acid which they considered formed in the reaction, and to which they gave the formula $H_2C_4O_3$. In beginning this investigation, Mr. O. R. Jackson and I thought it best at the outset to test experimentally the truth of the equation,

$$2C_4H_2Br_2O_3 + H_2O = C_4H_2O_3 + C_2HBr + 2CO_2 + 3HBr$$

which Schmelz and Beilstein had given as an expression of the reaction, and at the same time to determine the conditions most favorable to the formation of baric muconate. The qualitative

results we found to be precisely in accordance with their statements, and it was only necessary to study the reaction quantitatively. A weighed quantity of mucobromic acid was introduced into a flask fitted with reverse cooler, and dissolved in a little warm water. The upper end of the cooler was then connected with a series of wash-bottles which were filled with an ammoniacal solution of cuprous oxide, made by reducing an ammoniacal solution of pure cupric sulphate with metallic copper. The air in the apparatus was then displaced by pure hydrogen, a measured quantity of a standard solution of baric hydrate introduced into the flask, and heat applied. When the action appeared to be finished, we determined the weight of the baric carbonate which had been formed in the reaction, the weight of the baric carbonate which could be precipitated from the filtered solution by carbonic dioxide, and the weight of the baric muconate left on evaporation after washing out the baric bromide with cold water. In order to determine the amount of bromacetylen, we filtered off the voluminous precipitate of acetylen copper which had separated in the wash-bottles, acidified the filtrate, and precipitated the bromine with argentic nitrate.

The results which we obtained are given in the following table; in each case 2 grams of mucobromic acid were taken.

No.	BaO_2H_2 taken.	$BaCO_3$ by CO_2.	Br.	BaCO. formed.	"Baric muconate."
I.	1.994		0.372	0.57	
V.	2.971	trace	0.293	1.07	0.40
VI.	2.971	trace	0.333	1.05	0.55
II.	5.988	3.52	0.135	0.54	0.85
III.	5.942	3.25	0.146	0.50	0.87
IV.	5.942	3.40	0.128	0.53	0.97
VII.	8.044	5.75	0.135	0.47	0.95
VIII.	8.044	5.90	0.112	0.35	0.90

In order to compare these results more conveniently, we calculated from them the corresponding molecular ratios.

The following table contains the number of molecules of baric hydrate which we used in the various experiments for the decomposition of one molecule of mucobromic acid, the number of molecules of baric hydrate which actually entered into the reaction, and the fractions of a molecule of bromacetylen, carbonic dioxide, and baric muconate which were formed in each case. In accord-

ance with the results which we afterwards obtained, the muconate is here calculated as baric malonate.

No.	Baric hydrate. taken.	used.	Bromacetylen.	Carbonic dioxide.	"Baric muconate."
I.	1.50	1.50	0.60	0.37	
V.	2.24	2.24	0.47	0.70	0.20
VI.	2.24	2.24	0.54	0.69	0.28
II.	4.51	2.21	0.22	0.35	0.43
III.	4.48	2.35	0.24	0.33	0.44
IV.	4.48	2.25	0.21	0.35	0.49
VII.	6.07	2.30	0.22	0.31	0.48
VIII.	6.07	2.17	0.18	0.23	0.45

These results were sufficient to show that, in the decomposition by baric hydrate, we had to deal with at least two independent reactions; that one of these reactions led to the formation of carbonic dioxide and bromacetylen, while the second had for its chief product the sparingly soluble barium salt—the baric muconate of Schmelz and Beilstein. Moreover, it was evident that, in order to obtain the best yield of the latter salt, a large excess of baric hydrate should be employed.

In the preparation of the sparingly soluble barium salt, we used five or six molecules of baric hydrate to one of mucobromic acid. When the reaction appeared at an end, we precipitated the excess of baric hydrate with carbonic dioxide, and evaporated the filtered solution to a small volume. When this solution was slowly evaporated upon the water bath, we found, in accordance with the statements of Schmelz and Beilstein, that the salt separated in thin crusts which had no visible crystalline structure. If, however, the solution was boiled down rapidly over the lamp, at a certain point the salt suddenly separated in fine, silky needles, which were still further increased as the solution cooled. These crystals were well washed with cold water, redissolved in boiling water, and precipitated with plumbic acetate. In this way a granular lead salt was thrown down, which, when examined under the microscope, was seen to consist of well-formed rhombic plates. For analysis, the salt was dried at 110°.

I. 0.5939 gram substance gave 0.2434 gram CO_2 and 0.0470 gram of H_2O.

II. 0.3459 gram gave, by ignition with H_2SO_4, 0.3402 gram $PbSO_4$.

	Calculated for PbC_4O_3.	Calculated for $PbC_3H_2O_4$.	Found. I.	II.
C	15.84	11.65	11.18	
H	...	0.65	0.88	
Pb	68.32	66.99		67.22

It will be seen that the percentages found correspond closely with those required by plumbic malonate, and differ widely from those required by the formula of Schmelz and Beilstein.

The barium salt also agrees well with the description of baric malonate given by Heintzel[1] and Finkelstein.[2] The analyses we have made of the salt have given us too high a percentage of barium, although materially lower than that found by Schmelz and Beilstein.

I. 0.5212 gram of the salt, dried at 120°, gave 0.5214 gram $BaSO_4$.

II. 0.3455 gram of the salt, dried at 100°, gave 0.3159 gram $BaSO_4$.

III. 0.2139 gram of the salt, dried at 100°, gave 0.1956 gram $BaSO_4$.

	Calculated for $BaC_3H_2O_4.H_2O$.	Found. I.	II.	III.	Schmelz and Beilstein.
Ba	53.33	54.70	53.75	53.73	56.32

The result of Schmelz and Beilstein is here calculated for the hydrous salt. They found that the salt, when dried at 100°, lost 4.15 per cent. of water at 200°, and contained then 58.6 per cent. of barium.

From the lead salt we made the free acid by means of hydric sulphide, and found it very soluble in water or alcohol, less freely in ether. From aqueous solution it crystallized in irregular rhombic plates, occasionally in more compact prismatic forms. After several recrystallizations from water, and thorough drying over sulphuric acid, these crystals melted at 131.5–132°. This agrees with the melting point of malonic acid, as given by Heintzel, although it is somewhat lower than that more recently given by Pinner.[3] A combustion left no doubt of the identity and the purity of the acid.

[1] Ann. Chem. u. Pharm. **129**, 133. [2] Ann. Chem. u. Pharm. **133**, 343.
[3] Berichte der deutsch. chem. Gesellsch. **8**, 965.

0.3849 gram substance gave 0.4871 gram CO_2 and 0.1395 gram H_2O.

	Calculated for $C_3H_4O_4$.	Found.
C	34.61	34.51
H	3.85	4.03

The quantity of baric malonate which we obtained from mucobromic acid agreed with the results of our experiments upon a smaller scale, and amounted to nearly fifty per cent. of the theoretical yield. The mother liquors contained, beside baric bromide, baric formiate, whose presence could readily be established by qualitative tests.

Although the gaseous product formed by this decomposition with baric hydrate agreed closely in its qualitative reactions with bromacetylen, it seemed to us advisable to prove its identity a little more rigorously. We therefore passed the gas, diluted with hydrogen, into bromine and water. The crystalline solid which resulted we washed with dilute sodic hydrate, then with water, and finally recrystallized it from alcohol. Thus purified, it formed long, brilliant prisms, which melted at 54°. The melting point of pentabromethan is given by Lennox[1] as 48°; by Reboul,[2] 48–50°; by Limpricht and Delbrück,[3] 50–52°; and by Bourgoin,[4] 56–57°. The prismatic angle could readily be determined, and the measurement of several individuals gave as its mean value 104° 17′. Reboul gives the same angle in crystals of pentabromethan as 104° 20′, and Bourgoin as 104° 16′.

The identity of the substance was still further established by analysis.

0.1151 gram substance gave 0.2547 gram AgBr.

	Calculated for C_2HBr_5.	Found.
Br	94.12	94.17

After we had proved that malonic acid was one of the final products of the decomposition of mucobromic acid when boiled with an excess of baric hydrate, we attempted, by various modifications of the mode of decomposition, to isolate intermediate products, which might give us information concerning the nature of the reaction. After many unsuccessful experiments, we found that such products resulted from the action of alkalies at ordinary tempera-

[1] Lond. R. Soc. Proc. **11**, 257; Ann. Chem. u. Pharm. **122**, 122.
[2] C. R. **54**, 1229; Ann. Chem. u. Pharm. **124**, 267; Bull. Soc. Chim. 1862, 75.
[3] Ann. Chem. u. Pharm. **165**, 297.
[4] Ann. Chem. Phys. [5] **4**, 423; Bull. Soc. Chim. [2] **23**, 175, 257.

tures, and they were most conveniently studied when baric hydrate was employed.

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2$. If mucobromic acid is gradually added to a solution of baric hydrate containing a large excess of baric hydrate in suspension, it dissolves readily, and the crystals of baric hydrate at the same time gradually disappear. After a while a beautifully crystalline barium salt begins to separate, the amount of which increases rapidly as the acid is added. In order to prepare this salt, we found it best to add the mucobromic acid until one molecule had been used for every one and a half molecules of baric hydrate. At first we used two parts of crystallized baric hydrate and four of water to one part of mucobromic acid, but subsequently we reduced the amount of water one-half. After the necessary amount of mucobromic acid had been added in small portions, care being taken to prevent any elevation of temperature, the whole was allowed to stand for a short time, and the crystals which had separated were then filtered off on the pump. These were washed with a little cold water, exposed to carbonic dioxide until neutral in their reaction, and then recrystallized from water or diluted alcohol. From alcohol, the salt crystallized in pearly rhombic plates; from water, in irregular leafy forms, or, on slow evaporation, in massive aggregates of rhombic plates. When dried by exposure to the air, they lost nothing over sulphuric acid or when heated to 80°. At 100° they slowly lost in weight.

The air-dried salt gave on analysis the percentages required by the barium salt of a dibromacrylic acid.

I. 1.0621 gram of the salt gave 0.4745 gram CO_2 and 0.0780 gram H_2O.

II. 1.0363 gram of the salt gave 0.4609 gram CO_2 and 0.0743 gram H_2O.

III. 0.6187 gram gave, on ignition with H_2SO_4, 0.2415 gram $BaSO_4$.

IV. 0.6180 gram gave 0.2434 gram $BaSO_4$.

V. 0.5785 gram gave 0.2269 gram $BaSO_4$.

VI. 0.3522 gram gave 0.1381 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_2O_2)_2$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	12.10	12.19	12.14	...	...	...	...
H	0.34	0.82	0.80	...	...	...	...
Ba	23.03	...	...	22.95	23.15	23.05	23.05

Argentic Dibromacrylate, $AgC_3HBr_2O_2$. From the barium salt, or, better, from a solution of the free acid, the silver salt was made by the addition of argentic nitrate. It is precipitated in the form of fine, felted needles, even from a dilute solution of the acid; it may be recrystallized from hot water without any essential decomposition, and forms then long, flattened needles. The salt was dried over sulphuric acid for analysis.

I. 0.9755 gram substance gave 0.3890 gram of CO_2 and 0.0432 gram of H_2O.

II. 0.3200 gram substance gave, by the method of Carius, 0.3545 gram AgBr.

III. 0.7148 gram substance, precipitated with HBr, gave 0.4005 gram AgBr.

IV. 0.3668 gram gave, with HBr, 0.2056 gram AgBr.

Calculated for $AgC_3HBr_2O_2$.		Found.			
		I.	II.	III.	IV.
C	10.69	10.87	...	...	...
H	0.30	0.49	...	...	...
Br	47.47	...	47.14	...	...
Ag	32.05	...	...	32.18	32.20

Plumbic Dibromacrylate, $Pb(C_3HBr_2O_2)_2$. The lead salt is precipitated in pearly rhombic scales by the addition of plumbic acetate to a solution of the free acid. It is readily soluble in hot water, sparingly in cold. When dried over sulphuric acid *in vacuo*, it gave: —

I. 0.3232 gram substance gave 0.1289 gram CO_2 and 0.0230 gram H_2O.

II. 0.4060 gram gave 0.1858 gram $PbSO_4$.

III. 0.4908 gram gave 0.2230 gram $PbSO_4$.

Calculated for $Pb(C_3HBr_2O_2)_2$.		Found.		
		I.	II.	III.
C	10.82	10.86	...	...
H	0.30	0.79	...	...
Pb	31.13	...	31.27	31.05

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$. On neutralizing a solution of the acid with calcic carbonate, and concentrating the solution on the water bath, the calcium salt was obtained in clusters of radiating needles, tolerably soluble even in cold water. The

salt gradually effloresced over sulphuric acid, and lost its crystal water completely at 80–85°.

0.7342 gram of the air-dried salt lost, at 80–85°, 0.0695 gram of H_2O.

	Calculated for $Ca(C_3HBr_2O_2)_2.3H_2O$.	Found.
H_2O	9.78	9.47

0.4951 gram of the salt, dried at 80–85°, gave, on ignition with H_2SO_4, 0.1354 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)$.	Found.
Ca	8.03	8.04

Potassic Dibromacrylate, $KC_3HBr_2O_2$. The acid neutralized with potassic carbonate and evaporated gave, on cooling, crystals of the potassium salt. From neutral solutions it crystallizes in transparent, six-sided, clustered plates. If but a small amount of free acid is present, it crystallizes in fine, felted needles. Both forms are anhydrous, and do not lose in weight at 80°.

0.5506 gram gave, on ignition with H_2SO_4, 0.1792 gram K_2SO_4.

	Calculated for $KC_3HBr_2O_2$.	Found.
K	14.58	14.61

An acid salt much less soluble in water may be made by adding acid to a solution of the potassium salt. It crystallizes in long needles, which are anhydrous. The salt is not particularly stable, and the excess of acid may be washed out with ether. The salt was dried by exposure to the air, after several recrystallizations from hot water.

I. 0.6116 gram substance gave, on ignition with H_2SO_4, 0.1151 gram K_2SO_4.

II. 0.5395 gram of substance gave 0.0959 gram K_2SO_4.

	Calculated for $KC_3HBr_2O_2.C_3H_2Br_2O_2$.	Found. I.	Found. II.
K	7.85	8.45	7.98

Dibromacrylic Acid. From the pure barium salt we set free the acid by the addition of hydrochloric acid, and extracted it from the solution with ether. The ether left, upon evaporation, a white, crystalline acid, which was very soluble in alcohol, ether, or chloroform, and but sparingly soluble in benzol, carbonic disulphide, or ligroin. Under water, it melted at about 20°, dissolved in every

proportion on heating, and was but slowly volatilized with steam. The acid, when melted under water, could be made to crystallize either by cooling with ice or by the addition of a mineral acid. After recrystallization from benzol, it melted at 83–84°, and this melting point we were unable to raise by further recrystallization from this or other solvents.

Although our analyses left no doubt of the formula of the substance, they showed that it was still impure.

I. 1.3074 gram substance gave 0.7692 gram CO_2 and 0.1121 gram H_2O.

II. 0.9833 gram substance gave 0.5797 gram CO_2 and 0.0877 gram H_2O.

III. 0.2042 gram gave 0.3366 gram AgBr.

IV. 0.2447 gram gave 0.4044 gram AgBr.

V. 0.2083 gram gave 0.3453 gram AgBr.

VI. 0.2005 gram gave 0.3309 gram AgBr.

VII. 0.2132 gram gave 0.3517 gram AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
C	15.65	16.04	16.08	...	...	...	...	...
H	0.87	0.95	0.99	...	...	...	...	...
Br	69.56	...	...	70.15	70.33	70.53	70.23	70.20

Our results had sufficiently established the fact that a dibromacrylic acid was formed from mucobromic acid by the action of baric hydrate in the cold, but a more extended investigation of it was evidently needed to determine the nature of the impurity which was so difficult of removal. Since Wallach and Reincke[1] had shortly before announced that they were engaged in making from bromalid a dibromacrylic acid, which we thought probable, although upon very insufficient grounds, would prove to be identical with ours, we felt compelled for the moment to suspend our investigations. The other portions of the research afterward claimed so much attention that no study of the acid has yet been made sufficiently extended to establish the conditions essential to its preparation in a pure state. It has been found, however, that an acid melting at 84–85° contains but a slight excess of bromine (I.), and that the pure acid (II.) melts at 85–86°.

I. 0.2204 gram substance gave 0.3621 gram AgBr.

[1] Berichte der deutsch. chem. Gesellsch. **10**, 2128.

II. 0.2650 gram substance gave 0.4336 gram AgBr.

Calculated for $C_3H_2Br_2O_2$.		Found. I.	Found. II.
Br	69.56	69.90	69.65

For purposes of comparison, certain determinations of the solubility of the acid and its barium salt may find a place here, although they were not made with absolutely pure material, and are therefore subject to revision. In determining the solubility of the acid, the saturated solution, made according to the method of V. Meyer, was neutralized with baric carbonate, and the dissolved barium determined by precipitation with sulphuric acid.

I. 14.7798 grams of a solution, saturated at 20°, gave 0.4488 gram $BaSO_4$.

II. 8.6788 grams of a solution, saturated at 20°, gave 0.2630 gram $BaSO_4$.

According to these determinations, an aqueous solution of the acid, saturated at 20°, contains the percentages:

I.	II.
5.98	5.98

8.4992 grams of a solution of the barium salt, saturated at 20°, gave, on evaporation with H_2SO_4 and ignition, 0.1912 gram $BaSO_4$.

The aqueous solution of baric dibromacrylate, saturated at 20°, therefore contains 5.74 per cent. of the dry salt.

In studying the behavior of this dibromacrylic acid towards reagents, we have been able to use only the product melting at 83–84°, which may easily be obtained in any quantity desired. When boiled with an excess of baric hydrate, the acid is completely decomposed, baric carbonate is precipitated, bromacetylen set free, and at the same time baric malonate is formed in abundance. For complete identification, the baric malonate was converted into the lead salt, and the latter analyzed.

0.5179 gram of the salt, dried at 110°, gave, on ignition with H_2SO_4, 0.5062 gram $PbSO_4$.

Calculated for $PbC_3H_2O_4$.	Found.
66.99	66.79

The amount of baric malonate formed in this decomposition with an excess of baric hydrate was found to be forty-nine per cent. of the theoretical yield as the mean of two determinations.

The behavior of the acid towards hydrobromic acid was studied by Mr. C. F. Mabery. It is not altered by ordinary concentrated hydrobromic acid (b. pt. 126°), nor is it affected in the cold by an acid saturated at 0° ; but it forms an addition-product when heated with it for several hours at 100°. The reaction is by no means neat, and a large portion of the substance is charred. The tribrompropionic acid which is thus formed differs essentially in its melting-point (116–117°) and other physical properties from the acid melting at 93° mentioned by Linneman and Penl,[1] and recently more fully described by Michael and Norton ;[2] and also from the acid melting at 53°, which was obtained by Fittig and Petri,[3] by the action of hydrobromic acid upon their dibromacrylic acid. It is sparingly soluble in cold water, readily in hot, and may be crystallized without difficulty from hot water. It is readily soluble in alcohol or ether, somewhat less soluble in chloroform. From water it crystallizes in pearly scales, which melt at 116–117°. Argentic nitrate precipitates from an aqueous solution of the acid, the silver salt in clustered rhombic plates.

0.1892 gram of the acid gave 0.3453 gram AgBr.

	Calculated for $C_3H_2Br_3O_2$.	Found.
Br	77.16	77.64

If one molecule of bromine is added to dibromacrylic acid dissolved in chloroform, the color of the bromine gradually disappears, and after the lapse of some time tetrabrompropionic acid separates in large, well-formed crystals, which melt at 125°. This acid is at present under investigation in this laboratory.

One well-marked product of the decomposition of mucobromic acid by cold baric hydrate had been shown to be baric dibromacrylate ; it only remained to study the more soluble products of the reaction. In continuing the investigation with Mr. O. R. Jackson, the filtrate from the crystals of baric dibromacrylate was treated with carbonic dioxide to remove the excess of baric hydrate, filtered from the baric carbonate, and the filtrate evaporated at a gentle heat (40–50°). In the course of this evaporation, a certain amount of baric dibromacrylate crystallized out, which was removed from time to time. When the liquid had been reduced to about one-third its original volume, it was precipitated by the addition of

[1] Berichte der deutsch. chem. Gesellsch. 8, 1098. [2] Amer. Chem. Journ. 2, 18.
[3] Ann. Chem. u. Pharm. **195**, 73.

two volumes of alcohol. The bulky crystalline precipitate thus thrown down proved upon qualitative examination to consist chiefly of baric formiate. When purified by repeated precipitation from aqueous solution by alcohol and recrystallization from water, it showed the characteristic form of baric formiate.

0.3964 gram substance gave, on ignition with H_2SO_4, 0.4054 gram $BaSO_4$.

	Calculated for Ba $CHO_2)_2$.	Found.
Ba	60.36	60.13

The lead salt made from the barium salt crystallized in the characteristic form of plumbic formiate, and gave on analysis the required percentage of lead.

0.4149 gram of the salt gave, on ignition with H_2SO_4, 0.4221 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.50

In the alcoholic filtrate from the baric formiate, we were able to find, beside baric bromide, only a crystallizable barium salt, well marked by its qualitative reactions, but so unstable that we were not able to effect its purification. The behavior of this salt, and the analyses which we made of it in an impure state, led us to the conclusion that it was the barium salt of brompropiolic acid, formed by subtraction of hydrobromic acid from the dibromacrylic; and this view was subsequently proved to be correct by a study of the addition products which the corresponding acid formed with the halogens and the haloid acids.

Since all our attempts to isolate a pure salt from a solution containing baric bromide had proved unsuccessful, we attempted to take advantage of a remarkably stable molecular compound which the corresponding acid forms with dibromacrylic acid. This compound may readily be made by acidifying the baric hydrate solution of mucobromic acid, without removing the separated baric dibromacrylate, and extracting the solution with ether. The same compound, although in smaller quantity, may also be obtained, after that portion of the barium salt which separates spontaneously is removed. From dibromacrylic acid it may be made by the action of baric hydrate in the cold. For its preparation we usually have employed a solution of potassic, instead of baric, hydrate. The proportions which we have found most advantageous are 70

grams of potassic hydrate and 400 cc. of water to 100 grams of mucobromic acid. Care must be taken in adding the mucobromic acid, and also in the subsequent acidification with hydrochloric acid, that no sensible elevation of temperature takes place. When the solution is partially acidified, the acid potassium salt of dibromacrylic acid usually separates in abundance, but dissolves upon further addition of acid. The solution is then thoroughly extracted with ether; and this leaves on distillation a liquid residue, which, on cooling, gradually solidifies in large, well-formed, monoclinic (?) prisms. These are readily soluble in water, alcohol, ether, or chloroform, and may be purified by crystallization from hot benzol, or more conveniently by melting with a little water. Thus purified, the substance melts at 104–105°; and this melting point is not altered by repeated recrystallizations from various solvents.

I. 0.9023 gram substance gave 0.6440 gram CO_2 and 0.0850 gram H_2O.

II. 0.4403 gram substance gave 0.3157 gram CO_2 and 0.0433 gram H_2O.

III. 0.2263 gram substance gave 0.3386 gram AgBr.

IV. 0.2241 gram substance gave 0.3321 gram AgBr.

V. 0.2092 gram substance gave 0.3139 gram AgBr.

	Calculated for $C_6H_3Br_3O_4$.	Found.				
		I.	II.	III.	IV.	V.
C	19.00	19.43	19.54	...	...	...
H	0.79	1.05	1.09	...	...	...
Br	63.33	...	...	63.66	63.03	63.84

Although the percentages we have found show a considerable variation from those calculated for equal molecules of dibromacrylic and brompropiolic acids, they agree better with this than with any other formula equally simple; and, moreover, the qualitative behavior of the substance is such as to render this formula tolerably certain. Its aqueous solution gives, on the addition of plumbic acetate, an immediate crystalline precipitate of plumbic dibromacrylate.

0.3560 gram gave, on ignition with H_2SO_4, 0.1628 gram $PbSO_4$.

	Calculated for $Pb(C_3HBr_2O_2)_2$.	Found.
Pb	31.13	31.25

So also if it is neutralized with baric carbonate, the solution gives, on spontaneous evaporation, crystals of baric dibromacrylate, while in solution remains a much more soluble salt, with all the characters of baric brompropiolate. That this substance contains the brompropiolic acid is shown by the evolution of carbonic dioxide and bromacetylen when its aqueous evolution is boiled.

Starting with this molecular compound melting at 104–105°, we made various attempts to isolate the brompropiolic acid and its salts in a pure state. The barium salts of dibromacrylic and brompropiolic acids showed such marked differences in their solubility in water or in alcohol that we hoped through them to effect a complete separation of the two acids. We found, however, that it was difficult to obtain in this way a colorless salt of brompropiolic acid which appeared even tolerably pure. We therefore attempted to separate the two acids by converting them into their ethyl-ethers and submitting these to fractional distillation. We dissolved the molecular compound (m. pt. 104°) in absolute alcohol, added concentrated sulphuric acid, and warmed. The ethers soon separated in part, and were precipitated with water, washed with dilute sodic carbonate, and dried over fused calcic chloride. These mixed ethers had an extremely sharp, pungent odor, and their vapor attacked the eyes violently. On attempting to separate the two by distillation, we found that a large portion of the liquid was carbonized in each distillation, and that but one volatile product could be isolated. This was a mobile liquid, of an agreeable aromatic odor, which boiled between 209 and 215°, without any very noticeable decomposition. The portion of this which boiled between 212–214° was analyzed, and found to be essentially the ethyl-ether of dibromacrylic acid, although still impure. Since our chief object was to isolate the ether of the brompropiolic acid, and this had evidently been for the most part destroyed, the substance was not farther examined.

0.5235 gram of substance gave, on combustion, 0.4675 gram CO_2 and 0.1250 gram H_2O.

	Calculated for $C_3HBr_2O_2.C_2H_5$.	Found.
C	23.23	24.36
H	2.33	2.65

Finally, we attempted to separate the two acids by fractional saturation. Although the products thus obtained gave us analy-

tical results that were far from satisfactory, we found that the separation could be effected with tolerable precision, the brompropiolic acid being the stronger acid, and that this was the most convenient way of preparing material sufficiently pure for further work, in any considerable quantity. Pure substance melting at 104–105° was dissolved in water, and a little less than the calculated amount of baric carbonate was added. The clear solution was then freed as completely as possible from dibromacrylic acid by repeated extraction with ether, and the baric brompropiolate obtained by spontaneous evaporation.

Our analytical results show that the material analyzed was not pure, and yet they leave no doubt as to its nature.

I. 0.6974 gram of substance, dried over H_2SO_4, gave 0.3968 gram CO_2 and 0.0347 gram H_2O.

II. 0.3060 gram of substance, dried over H_2SO_4, gave 0.1657 gram $BaSO_4$.

III. 0.1829 gram of substance, dried over H_2SO_4, gave 0.0973 gram $BaSO_4$.

IV. 0.4325 gram of substance, dried over H_2SO_4, gave 0.2305 gram $BaSO_4$.

	Calculated for $Ba(C_3BrO_2)_2$.	Found.			
		I.	II.	III.	IV.
C	16.63	15.52	...	...	...
H	...	0.55	...	...	...
Ba	31.63	...	31.84	31.27	31.32

We have been unable to make any satisfactory determinations of the water of crystallization, since the salt cannot be heated, and even on standing over sulphuric acid in the cold it is slowly decomposed. The salt when crystallized from water probably contains four molecules of water.

I. 2.1104 gram of the air-dried salt lost over sulphuric acid 0.2803 gram.

II. 0.9828 gram of air-dried substance lost over H_2SO_4 0.1316 gram.

	Calculated for $Ba(C_3BrO_2)_2.4H_2O$.	Found.	
		I.	II.
H_2O	14.26	13.28	13.39

In one instance the salt precipitated from alcoholic solution by the addition of ether was found to contain but a single molecule of water.

1.0639 gram of air-dried salt lost over H_2SO_4 *in vacuo* 0.0458 gram.

	Calculated for $Ba(C_3BrO_2)_2.H_2O$.	Found.
H_2O	3.99	4.30

The salt usually crystallized, on the slow evaporation of its aqueous solution, in small, oblique prisms ; but it sometimes separated, on long standing, in more compact, clustered, rhombic plates. When dry, it is decomposed quite rapidly at 50°, and deflagrates at about 125°. In aqueous solution it is recomposed on boiling, with the precipitation of baric carbonate and the evolution of carbonic dioxide and bromacetylen. From solutions containing an excess of the acid, a somewhat more stable salt separates in fine, felted needles, less soluble in water than the neutral salt. This would seem to be an acid salt, corresponding to the acid potassium salt of dibromacrylic acid ; but we could obtain no satisfactory analytical results.

When argentic nitrate is added to a solution of the barium salt, or of the free acid, a white, amorphous silver salt is precipitated, and at the same time if the solution is concentrated the evolution of carbonic dioxide is noticed. The precipitate turns yellow on washing, and is evidently still further decomposed on drying. When gently warmed with water, it is slowly decomposed ; but, when suddenly heated nearly to 100°, it explodes violently, with the separation of large quantities of carbon. In a dry state it explodes when heated to about 75°. In dilute nitric acid it dissolves at first ; but the solution soon grows turbid, smells strongly of bromacetylen, and argentic bromide is precipitated. One could hardly expect trustworthy results from the analysis of so unstable a substance. One silver determination, however, showed that it must be considered a derivative of bromacetylen, rather than of brompropiolic acid.

0.2313 gram of substance, dried over H_2SO_4 *in vacuo*, gave 0.1975 gram AgBr.

	Calculated for AgC_3BrO_2;	for AgC_2Br.	Found.
Ag	42.19	50.94	49.05

Although the barium salt had given unsatisfactory results on analysis, we made from it the acid, and hoped then to be able to effect its purification. We therefore precipitated the barium from a cold, aqueous solution, with a slight excess of sulphuric acid, and

extracted the acid from the filtered solution with ether. We obtained in this way long, slender prisms, extremely soluble in water, alcohol, or ether, readily in chloroform or benzol, more sparingly in carbonic disulphide, and but slightly soluble in ligroin. The crystals obtained from aqueous solution by spontaneous evaporation appeared to contain water of crystallization. When pressed with paper they melted at 60–65°; but over sulphuric acid they soon became opaque, and the melting point had risen to 80° or over.

We attempted the purification of the acid by repeated recrystallization from ligroin to which a little ether had been added. The long, silky needles thus obtained melted at 86°, but gave on analysis no satisfactory results (I. and II.). Although the acid was blackened and apparently completely decomposed at a temperature but little over 100°, we found that it could be sublimed readily between watch-glasses at steam heat. The melting point was, however, lowered rather than raised, by successive sublimations, and analyses (III. and IV.) of the sublimed product gave too high a percentage of bromine.

I. 0.3010 gram substance gave 0.4025 gram AgBr.
II. 0.1198 gram substance gave 0.1582 gram AgBr.
III. 0.2010 gram substance gave 0.2580 gram AgBr.
IV. 0.1820 gram substance gave 0.2339 gram AgBr.

	Calculated for C_3HBrO_2.	Found.			
		I.	II.	III.	IV.
Br	53.69	56.90	56.21	54.63	54.69

The acid is decomposed, with the formation of carbonic dioxide and bromacetylen, on boiling its aqueous solution. When heated with an excess of baric hydrate, baric carbonate is precipitated, bromacetylen is evolved, and at the same time baric malonate is formed in abundance. It unites with dibromacrylic acid immediately to form the characteristic addition-product. An ethereal solution containing a mixture of the two acids, approximately in molecular proportions, gave on evaporation a substance which, without purification, melted at 103°. With the halogens and haloid acids, it forms addition products with the greatest readiness. The substituted acrylic acids which are thus formed, according to the equations,—

$$C_3HBrO_2 + HX = C_3H_2BrXO_2$$
$$C_3HBrO_2 + X_2 = C_3HBrX_2O_2,$$

are easily purified, and their formation can leave no doubt of the nature of the brompropiolic acid. Several of these acids will be described later in this paper.

The decomposition of mucobromic acid by baric hydrate, under the conditions described, may be expressed by the following equations. The first action would seem to be the assimilation of a molecule of water and the formation of dibromacrylic and formic acids.

$$C_4H_2Br_2O_3 + H_2O = C_3H_2Br_2O_2 + CH_2O_2.$$

This action is immediately followed, even in the cold, by the subtraction of hydrobromic acid,—

$$C_3H_2Br_2O_2 - HBr = C_3HBrO_2.$$

The brompropiolic acid is then either decomposed by heat,—

$$C_3HBrO_2 = C_2HBr + CO_2,$$

or is converted into malonic acid,—

$$C_3HBrO_2 + 2H_2O = C_3H_4O_4 + HBr.$$

Since a large percentage of dibromacrylic acid was converted into brompropiolic acid in this reaction, and it had previously been proved that a portion of the mucobromic acid entirely escaped decomposition when the proportion of baric hydrate was materially lessened, I recently attempted to increase the yield by reversing the mode of procedure. I therefore added baric hydrate, gradually, to mucobromic acid suspended in a little water; taking care, after the acid was neutralized, to make the solution but slightly alkaline, and to wait until it was again neutral before further addition. I found, however, that an entirely different reaction had taken place under these conditions, and that among the products of this reaction little or no dibromacrylic acid could be found. This decomposition is at present under investigation in this laboratory, and all discussion of the results we have already obtained must therefore be reserved for a subsequent paper.

(*To be continued.*)

XI.—ON THE DIIODBROMACRYLIC AND CHLORBROMACRYLIC ACIDS.[1]

BY C. F. MABERY AND RACHAEL LLOYD.

The readiness with which brompropiolic acid unites with the halogens and the haloid acids to form members of the acrylic acid series has been described by Prof. H. B. Hill,[2] and certain of these addition products have been studied in detail by him and one of us.[3]

The products which result by the action of iodine and of hydrochloric acid on brompropiolic acid will be described in this paper.

DIIODBROMACRYLIC ACID, $C_3I_2BrO_2H$.

Diiodbromacrylic acid is formed when brompropiolic acid is allowed to stand for some time with a solution of iodine in ether. As this method of preparation was found to be somewhat tedious from the length of time required to complete the reaction, we tried the effect of raising the temperature. Brompropiolic acid, with a slight excess over the calculated weight of iodine and five parts by weight of ether, was heated for two hours under a return condenser on the water bath. The residue left after the evaporation of the ether was extracted with successive portions of warm water, and the solution concentrated by evaporation. Diiodbromacrylic acid was deposited from this solution, on cooling, in glistening plates, which were purified by recrystallization from hot water.

The yield of pure product by this method has been about sixty per cent. of the amount theoretically required. The mother liquors of the first crystallization gave by evaporation an oily product, which solidified on standing, but which could be purified only with considerable difficulty. This substance crystallizes in flat, white, six-sided plates, very sparingly soluble in cold water, readily in hot, and very soluble in ether, alcohol, carbonic disulphide, and ligroin. It melts at 160°, and sublimes slowly at higher temperatures, apparently unchanged. A yellow coating is formed on the surface when it is exposed to the action of light, yet the decomposition by nitric acid in the estimation of the halogens is not complete below 300°.

[1] Communicated by the Authors. This research was conducted in connection with the Summer Course of Instruction in Chemistry at Harvard College. C. F. M.

[2] Berichte der deutsch. chem. Gesellsch. 12, 660.

[3] Amer. Acad. Proc. 16, 211.

The following results were obtained by analysis:

0.5188 gram substance gave 0.1682 gram CO_2 and 0.0180 gram H_2O.

0.2004 gram substance gave by Carius' method 0.3276 gram $AgI+AgBr$.

	Calculated for $C_3I_2BrO_2H$.	Found.
C	8.93	8.84
H	.25	.39
I_2+Br	82.87	82.96

The solubility in cold water was determined by the method of V. Meyer. The filtered solution was neutralized with baric carbonate, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 11.7286 grams solution gave 0.0707 gram $BaSO_4$.

II. 13.3239 grams solution gave 0.0793 gram $BaSO_4$.

The solution, saturated at 20°, contains, therefore, the percentages:

I.	II.
2.08	2.05

Hence diiodbromacrylic acid requires for solution 48.37 parts water at 20°.

Salts of Diiodbromacrylic Acid.

Baric Diiodbromacrylate, $Ba(C_3I_2BrO_2)_2.4H_2O$. A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. The salt crystallized, on cooling, in flat prisms arranged in stellate groups. It is very soluble in hot, less soluble in cold, water.

I. 0.8805 gram air-dried salt gave 0.0638 gram H_2O at 80°.

II. 0.8981 gram air-dried salt gave 0.0629 gram H_2O at 80°.

III. 0.8049 gram anhydrous salt gave 0.2002 gram $BaSO_4$.

	Calculated for $Ba(C_3I_2BrO_2)_2.4H_2O$.	Found. I.	Found. II.
H_2O	7.11	7.24	7.00

	Calculated for $Ba(C_3I_2BrO_2)_2$.	Found.
Ba	14.55	14.62

To determine the solubility in cold water, a hot solution was kept at 20° for four hours, with occasional stirring. The filtered solution was evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 3.2417 grams solution gave 0.1218 gram $BaSO_4$.

II. 7.0500 grams solution gave 0.2665 gram $BaSO_4$.

This solution contains, therefore, the following percentages:

I.	II.
15.17	15.26

Taking the mean of these results, this salt requires for solution 6.571 parts water at 20°.

Calcic Diiodbromacrylate, $Ca(C_3I_2BrO_2)_2$. This salt was prepared by neutralizing a solution of the acid with calcic carbonate, and evaporating the filtered solution. The salt crystallizes in branching needles, which are very soluble in water.

0.5995 gram of the air-dried salt lost 0.0031 gram at 80°.

This was probably due to the presence of a trace of hygroscopic moisture.

0.5964 gram of the salt, dried at 80°, gave 0.0945 gram $CaSO_4$.

	Calculated for $Ca(C_3I_2BrO_2)_2$.	Found.
Ca	4.74	4.66

Argentic Diiodbromacrylate, $AgC_3I_2BrO_2$. Argentic nitrate, added to a solution of the acid, caused a voluminous precipitate of the silver salt, which was washed and dried over sulphuric acid for analysis. It forms oblique prisms, very slightly soluble in cold water, but readily soluble in dilute nitric acid.

0.9585 gram salt gave 0.2677 gram AgCl.

	Calculated for $AgC_3I_2BrO_2$.	Found.
Ag	21.17	21.02

Potassic Diiodbromacrylate, $KC_3I_2BrO_2.2H_2O$. A solution of the acid was neutralized with potassic carbonate, and evaporated on the water bath. On cooling, the salt separated in the form of oblique prisms, which are quite soluble in water.

1.8818 gram of the air-dried salt gave 0.1381 gram H_2O at 80°.

1.7460 gram anhydrous salt gave 0.3347 gram K_2SO_4.

	Calculated for $KC_3I_2BrO_2.2H_2O$.	Found.
H_2O	7.55	7.33

	Calculated for $KC_3I_2BrO_2$.	Found.
K	8.87	8.50

Chlorbromacrylic Acid, $C_3ClBrO_2H_2$.

Chlorbromacrylic acid may be made by the action of ordinary fuming hydrochloric acid on brompropiolic acid. This reaction, however, takes place slowly in the cold; and, although the application of heat causes a more rapid formation of the chlorbromacrylic acid, it produces a secondary decomposition which renders the purification of the product somewhat difficult. We therefore tried the action of hydrochloric acid saturated at 0°. The acid solution soon became filled with crystals of the addition product; and after standing twenty-four hours the reaction was complete. The excess of hydrochloric acid was removed by decantation, and by pressure between folds of filter paper, and the chlorbromacrylic acid was purified by crystallization from hot water. It separates as an oily liquid from a hot aqueous solution; but when nearly cold it crystallizes, forming elongated, flat prisms or needles.

This acid melts at 70°, and sublimes quite freely at a somewhat higher temperature. It is much more soluble in hot than in cold water, and readily soluble in ether, alcohol, benzol, and carbonic disulphide. Its composition was determined by the following analyses:—

0.4462 gram substance gave 0.3126 gram CO_2 and 0.0337 gram H_2O.

0.1792 gram substance gave, by the method of Carius, 0.3186 gram AgCl+AgBr.

	Calculated for $C_3ClBrO_2H_2$.	Found.
C	19.40	19.11
H	1.08	.84
Cl+Br	62.26	61.94

The solubility of this acid in cold water was determined by the same method as the diiodbromacrylic acid.

I. 11.6861 grams solution gave 0.4178 gram $BaSO_4$.

II. 14.4534 grams solution gave 0.5264 gram $BaSO_4$.

The solution, saturated at 20°, contains the percentages:

I.	II.
5.69	5.80

The mean of these results gives 17.41 parts as the quantity of water required for solution at 20°.

Salts of Chlorbromacrylic Acid.

The salts of this acid were made by the same methods as the corresponding salts of diiodbromacrylic acid.

Baric Chlorbromacrylate, $Ba(C_3ClBrO_2H)_2.2H_2O$. This salt crystallizes in flattened prisms, which belong apparently to the monoclinic system. Its composition was established by the following analyses:

I. 0.3730 gram air-dried salt gave 0.0263 gram H_2O at 80°.

II. 0.6283 gram air-dried salt gave 0.0437 gram H_2O at 80°.

III. 0.3467 gram anhydrous salt gave 0.1606 gram $BaSO_4$.

IV. 0.4468 gram anhydrous salt gave 0.2053 gram $BaSO_4$.

	Calculated for $Ba(C_3ClBrO_2H)_2.2H_2O$.	Found.	
		I.	II.
H_2O	6.64	7.05	6.96

	Calculated for $Ba(C_3ClBrO_2H)_2$.	Found.	
		III.	IV.
Ba	27.07	27.23	27.02

The solubility in cold water was determined by the method of V. Meyer.

I. 2.8936 grams solution gave 0.1914 gram $BaSO_4$.

II. 5.1385 grams solution gave 0.3378 gram $BaSO_4$.

From these results the following percentages were calculated:

I.	II.
14.06	14.28

This salt, therefore, requires for solution 6.985 parts of water at 20°

Calcic Chlorbromacrylate, $Ca(C_3ClBrO_2H)_2.4H_2O$. This salt forms branching needles, which are very soluble in hot, less soluble in cold, water.

I. 0.4981 gram air-dried salt gave 0.0762 gram H_2O at 80°.
II. 0.6211 gram air-dried salt gave 0.0956 gram H_2O at 80°.
III. 0.4219 gram anhydrous salt gave 0.1424 gram $CaSO_4$.
IV. 0.5096 gram anhydrous salt gave 0.1713 gram $CaSO_4$.

	Calculated for $Ca(C_3ClBrO_2H)_2.4H_2O$.	Found. I.	II.
H_2O	14.97	15.30	15.39

	Calculated for $Ca(C_3ClBrO_2H)_2$.	Found. III.	IV.
Ca	9.78	9.93	9.87

Argentic Chlorbromacrylate, $Ag(C_3ClBrO_2H)_2$. This salt was precipitated by the addition of argentic nitrate and ammonic hydrate to a solution of the acid. It forms microscopic needles, which are almost insoluble in cold water.

I. 0.2760 gram salt gave 0.1337 gram AgCl.
II. 0.3445 gram salt gave 0.1668 gram AgCl.

	Calculated for $Ag(C_3ClBrO_2H)$.	Found. I.	II.
Ag	36.93	36.47	36.88

Potassic Chlorbromacrylate, KC_3ClBrO_2H. This salt forms clusters of irregular, pointed, anhydrous prisms, which are less soluble in cold than in hot water.

0.5346 gram salt, dried at 80°, gave 0.2132 gram K_2SO_4.

	Calculated for KC_3ClBrO_2H.	Found.
K	17.49	17.91

The addition of bromine to chlorbromacrylic acid takes place very readily at the ordinary temperature, with the formation of chlortribrompropionic acid. A solution of the acid in chloroform was allowed to stand several days, with somewhat more than the calculated weight of bromine. Chlortribrompropionic acid separated from this solution in large prismatic crystals, which after crystallization from carbonic disulphide melted at about 98°. This acid will be submitted to a more extended study.

ON MICROLITE FROM AMELIA CO., VIRGINIA.

By F. P. Dunnington.

The mineral which is the subject of this examination was collected at the mica mines, two miles north of Amelia C.H., by Prof. W. M. Fontaine of this University, who gives the following notes of its occurrence and associations:

"This mineral occurs with others imbedded in a vein of 'Gigantic Granite,' (so called because of the essential minerals of the granite being crystallized in large masses) which is enclosed in gneiss and mica schist, with the general characters of the Montalban series. Schorl is very abundant in the adjoining wall-rock.

"The associated minerals are as follows:

"Beryl, abundant, sometimes in large crystals eight to ten inches in diameter; fluorite and columbite, not uncommon; amethystine quartz, occasional; apatite, rare. In addition to which are the large crystal masses composing the vein, quartz, orthoclase[1] and mica (of which last the sheets are frequently three feet across, and for which the vein is worked)."

Prof. Fontaine presumed the mineral in question would prove of interest, and handed it over to me for further examination, the result of which is as follows:

It is found in single crystals varying in dimensions from one-tenth to three-quarters of an inch, and in larger crystalline masses of which one was obtained weighing *eight pounds*. It occurs crystallized in octahedra of the Isometric system, some of the edges of which measure two centimetres; the face 1 is principally developed, and with it are the truncations made by O, 3-3 and *i* (Dana).

It has the following properties: Hardness, a little less than 6; specific gravity, 5.656; lustre, glistening resinous; color, wax yellow to brown; streak, pale ochreous yellow; subtranslucent; fracture conchoidal and very brittle.

Heated in a closed tube it decrepitates and gives off a little water. When ignited it glows momentarily as if taking fire. Before the blow-pipe it colors the flame a reddish yellow, is infusible, and on cooling is colored pale yellow and is without lustre. With the borax bead and also with that of salt of phosphorus, in both flames it gives a glass, yellowish when hot, colorless when cold. In both flames the saturated bead of salt of phosphorus is yellow when hot and greenish-yellow when cold. It is not attacked by strong

[1] Ratio of potash to soda=11 to 4.—F. P. D.

hydrochloric acid, but is decomposed slowly by concentrated sulphuric acid and also by fusion with caustic potash. It is readily decomposed by fusion with acid potassium sulphate. Fused with potassium nitrate and sodium carbonate, it does not give the manganese reaction. The moist metallic acids boiled with hydrochloric acid and tin afford a pale blue color.

The finely pulverized mineral was fused at a low red heat in a platinum crucible with eight parts of acid potassium sulphate. Four portions of about two grams each were thus fused, and all the constituents except the acids, alkalies and water, were then determined from the sum of these = 8.3370 grams of the mineral.

The metallic acids, insoluble in dilute hydrochloric acid, were well washed and then digested with yellow ammonium sulphide and washed, and then *separately* washed with dilute hydrochloric acid and finally washed with water. The oxides of tin and tungsten obtained from the ammonium sulphide solution were weighed together, then fused with sodium carbonate and a little potassium cyanide and washed. The tin dissolved out by hydrochloric acid, reprecipitated by hydrogen sulphide, washed, ignited and weighed, the tungsten being obtained by difference.

The insoluble metallic acids were treated with hydrofluoric acid and acid potassium fluoride, HKF_2, and the double salt, $2KF.TaF_5$, crystallized out according to Marignac's process; the crystals obtained were washed free of niobium and then dissolved and recrystallized. The washings and mother liquors were evaporated to a small bulk, and the crystals so obtained purified as before, and finally the filtrate again treated as before, there being obtained from one portion:

Ta_2O_5, 4.844. Sp. gr.=7.77, and after prolonged ignition=7.96.
[1] Nb_2O_5, .558.
giving the ratio 8.68 to 1.

And from another portion:

[2] Ta_2O_5, 5.189
Nb_2O_5, .577. Sp. gr. 4.20, and after prolonged ignition=4.23, giving the ratio 9 to 1.

The mean of these determinations gives the ratio by weight:

$$Ta_2O_5 \text{ to } Nb_2O_5 = 8.84 \text{ to } 1.$$

If these oxides when mixed do not change their volume on ignition, the mixed acids as separated should have had sp. gr.=less

[1] Containing some Ta_2O_5. [2] Containing some Nb_2O_5.

than 7.6, whereas after prolonged ignition they had sp. gr.=7.86. I propose therefore to further examine this apparent combination of so closely related elements.

All the above specific gravities were taken between 11° and 14° C., and referred to water at this temperature.

The cerium metals proved to be present in too small amount to admit of accurate separation; they consist in about equal portions of cerium and didymium, and probably entirely of these, as lanthanum was not identified.

None of the lines attributed to erbium were found with the earths of the yttria group.

A portion dissolved in sulphuric acid under carbon dioxide decolorized a very little potassium permanganate corresponding in amount to and probably due to the cerium as cerous oxide (Ce_2O_3), therefore the uranium and iron are taken as Ur_2O_3 and Fe_2O_3.

Fluorine was estimated by the volumetric method of Mr. S. L. Penfield,[1] and since, in order to decompose the mineral, the sulphuric acid was heated to 175° C. and for many hours, I took special precautions to condense the volatilized sulphuric acid and then deducted the minute amount of sulphuric acid found in the titrated liquid.

The water was given off below a red heat.

No trace of lead or of manganese was found.

The analysis gave the following results:

Ta_2O_5	68.43
Nb_2O_5	7.74
WO_3	.30
SnO_2	1.05
CaO	11.80
MgO	1.01
BeO	.34
U_2O_3	1.59
Y_2O_3	.23
Ce_2O_3, Di_2O_3	.17
Al_2O_3	.13
Fe_2O_3	.29
Na_2O	2.86
K_2O	.29
F	2.85
H_2O	1.17
	100.25
Deduct O replaced by F	1.20
	99.05

[1] This Journal, **1**, 27.

Considering the bases as replacing equivalent amounts of calcium and neglecting the water, we have the following atomic relations:

Ca	Ta	Nb	Sn & W	F	O
32.9	30.9	5.8	.83	15	118.6

If we exclude the Fe_2O_3 and Al_2O_3 as uncombined, as they most probably are, the following formula may be deduced:

$$\left\{\begin{matrix} 3(Ca_2Ta_2O_7)+NbOF_3 \\ m(CaWO_3) \end{matrix}\right.$$

It may be remarked that in *most* of the reported analyses of pyrochlore, the fluorine and alkaline metals nearly correspond in number of atoms, which is clearly not so in this case, while the relation between the niobium and fluorine points to the association of these elements under the familiar form of $NbOF_3$.

To some of the analyses of pyrochlore, considered by Prof. C. Rammelsberg in his extended paper[1] on tantalates and niobates, he assigns the formula:

$$\left\{\begin{matrix} m(R_2Nb_2O_7) \\ n(RTiO_3) \\ o(NaF) \end{matrix}\right.$$

From the results of the above analysis and also from its crystalline habit, it therefore appears that this mineral is the one which has been described by Prof. C. U. Shepard as microlite, although it proves to have a composition different from that originally supposed by him, and corresponding to that suggested by Prof. Brush, viz: essentially a calcium tantalate.

The minute size of the crystals in which it was previously found fully warranted the name microlite, but in view of the present facts it appears rather inappropriate.[2]

UNIVERSITY OF VIRGINIA, Apr. 1881.

[1] Journal Chem. Soc. Ser. 2, **10**, 203.

[2] A private communication from Prof. E. S. Dana informs me of a recent analysis by Nordenskiöld, of a mineral from Utö, in size of crystals a true microlite, who found in it: $Ta_2O_5(Nb_2O_5)$, 77.3; SnO_2, 0.8; CaO. 11.7; MuO, FeO, 7.7; MgO, 1.8; total, 99.3. F. P. D.

ON THE CONDUCT OF FINELY DIVIDED IRON TOWARDS NITROGEN.

By Ira Remsen.

A recent writer[1] states that the method of Lassaigne for the detection of nitrogen in bodies containing carbon is not applicable to compounds in which sulphur is present. He claims that the sulphur gives rise to the formation of sulphocyanide, and that this is overlooked, as the solutions are strongly acid. A list of compounds is given in which nitrogen can not be detected. It includes taurine, sulpho-urea, sulphocyanide of potassium, and the "amides of the sulphonic acids." In such cases it is recommended to fuse the bodies with sodium and pure iron, instead of sodium alone, as is customary. The sulphur forms sulphide of iron, and the nitrogen forms the cyanide and can easily be detected.

As I have repeatedly used the ordinary method for the detection of nitrogen in compounds containing sulphur, and have in some cases relied upon the results reached, I undertook an examination of the subject thus opened, and I have been led to conclusions directly opposed to those of the writer referred to. At the same time certain interesting observations have been made on the conduct of pure iron, reduced by hydrogen, towards nitrogen.

As regards the statement that the method of Lassaigne is not applicable to compounds containing sulphur, I am prepared to give this an unqualified denial. I have examined every one of the substances mentioned by the writer, with the exception of cystine, and have in each case without the slightest difficulty obtained the precipitate of Prussian blue. I have also examined a large number of other substances, and have never experienced difficulty in getting the result looked for. Then, further, the fact that sulphocyanide of sodium or potassium itself breaks up under the influence of heat in the presence of an alkaline metal shows clearly that, even if this salt is formed as is claimed and as is probable, the detection of the nitrogen can not be interfered with by the presence of sulphur.

Having shown beyond a doubt that the conclusion I had drawn with reference to a certain compound, that it contained no nitrogen,

[1] Berichte d. deutsch. chem. Gesell. **12**, 2316.

is correct, I nevertheless fused a small specimen of this compound with sodium and iron by hydrogen, and was astonished to find that, on extracting the fused mass with water, filtering and then adding successively ferric and ferrous salts and hydrochloric acid, the blue precipitate revealing the presence of nitrogen was distinctly formed. I repeated the experiments a number of times, but always with practically the same result. In every case the blue precipitate was formed, though in some cases it seemed to be formed in larger quantity than in others. The variations in quantity were, however, not striking.

I now took other non-nitrogenous organic substances than the one which was in question and tested these. The two purest specimens in this laboratory at the time were one of the double tartrate of potassium and sodium which had been recrystallized a large number of times, and one of cane sugar which had been repeatedly recrystallized from alcohol. These two specimens may certainly be regarded as in the strictest sense chemically pure. Both of these substances gave the reaction for nitrogen distinctly. Of all the substances experimented upon, the pure double tartrate seemed to be best adapted to the purpose, and in continuing the experiments I have since always employed this particular pure specimen to furnish the carbon.

The question naturally suggests itself, whence comes the nitrogen in these reactions? I at first suspected the iron by hydrogen, and my suspicions were increased when, on inquiring into the history of the specimen used, I found that it had been made from ferric hydroxide precipitated by ammonia. To be sure the hydroxide had been washed with the greatest care and had afterward of course been ignited in a current of hydrogen, and it did not seem probable that ammonia or any compound of ammonia and iron could be retained; but still, there was the nitrogen, and it appeared at least possible that it was actually contained in the iron. To test this point ferric hydroxide was precipitated from a solution of the pure chloride by means of sodium carbonate and washed out until no test for sodium could be obtained. This precipitate was then divided into two parts, one of which was dried at once, and the other boiled for some hours with a solution of ammonium carbonate and ammonia. The latter was then washed out, no special precautions being taken to remove all the ammonium salts, and afterward dried. Both specimens were separately reduced in a

current of purified and dried hydrogen. *Both gave the test for nitrogen*, and indeed the one from which all ammonium compounds had been carefully excluded seemed to give the test better than the other.

Another specimen of iron by hydrogen which has been in the collection of chemicals of this laboratory for five years, and which does not take fire by contact with the air, failed to give the nitrogen test. This led me to think that possibly the nitrogen is not contained in the iron, but is absorbed from the air, and that the power to absorb nitrogen in this way is connected with the active condition of the iron. Both the specimens above referred to, which in the active condition readily and invariably gave the test for nitrogen, were allowed to stand for a short time in contact with the air and were then again tested. *Neither gave the reaction.* The same experiment was performed with the specimen of iron by hydrogen first used, and which had been preserved under ether. A portion of this was allowed to stand over night exposed to the air and then gave no indication of the presence of nitrogen. These results make it appear extremely probable that the nitrogen detected when active iron is used is really absorbed from the air. But if this is so, then more thorough contact of the heated reagents with the air ought to increase the quantity of cyanide formed. All the experiments thus far mentioned were performed in test tubes, and of course very little air came in contact with the substance at the bottom of the tube. On heating the necessary mixture in a crucible, however, violent combustion of the sodium took place and no reaction for nitrogen was obtained. To prevent this combustion, a mixture of iron by hydrogen, double tartrate of sodium and potassium and metallic sodium was placed in a hard glass tube, and dry hydrogen passed through while gentle heat was applied to drive off water. Then nitrogen was passed slowly over the mixture, while at the same time it was heated to redness. This process was continued for about ten minutes, when, on allowing the tube to cool, the contents were extracted with water, filtered and treated in the usual manner. To my surprise, *a very large precipitate of Prussian blue was formed*, much larger in proportion than in any previous experiment. The result is so striking that the experiment is well adapted to serve the purpose of a lecture experiment, illustrating the formation of cyanogen from the nitrogen of the air. There can be no doubt that the nitrogen

is really absorbed from the air. The quantity of the precipitate obtained in the last experiment was so great as to exclude the supposition that the nitrogen could have been present in the substances used. Then, further, the fact that the active iron, which readily gives the test for nitrogen, does not give the test after it has been exposed to the air and become oxidized, is a clear indication that the active condition of the iron is an important factor in the process and that the nitrogen can not be in combination with the iron. For, if it were, it is difficult to understand how the spontaneous oxidation of the iron could remove it. The heat evolved can scarcely be sufficient to decompose any nitrogen compound present, for the iron is heated to a much higher temperature in the course of its preparation, and the possible nitrogen compound must have been decomposed by this first application of heat.

I have thus far performed no quantitative experiments, and there are obvious difficulties in the way of making these exact. As it is intended soon to continue the experiments, however, an attempt will be made to determine as nearly as possible how much nitrogen can be taken up and combined chemically by given weights of the reagents. Some other points of interest will also be taken up. Thus, in attempting to exclude the air from the vessels in which the reactions took place, hydrogen was used, and the nitrogen test was not obtained. But on testing a nitrogenous substance (hippuric acid) in the same way, very little evidence of nitrogen was obtained. It would, hence, appear that the test can not be applied in an atmosphere of hydrogen, or that the cyanide is decomposed when heated in hydrogen. On the other hand, Marchand[1] has stated that hydrogen does not interfere with the application of the test.

As a result of the experiments described in this paper, it may be stated with confidence that *when iron by hydrogen and certain non-nitrogenous organic substances are heated together with metallic sodium in an atmosphere of nitrogen, a cyanide is readily formed.* The action is, of course, similar to that which takes place in blast-furnaces and which gives rise to the formation of cyanide of potassium. In the latter case, the carbonate of potassium from the burning of the fuel furnishes the potassium. Nitrogen is always present in large quantity, and the iron is constantly passing from the state of oxide to that of the metal.

[1] Journal prak. Chemie, **49**, 355.

Marchand some years ago showed[1] that steel when heated with carbon and potassium can take up nitrogen. It had been previously stated by Schafhäutl[2] that steel always contains nitrogen. The experiments of Marchand made this statement appear improbable though they did not disprove it. Indeed, later a discussion arose in France on the same subject. Fremy claimed that not only is nitrogen always present in steel, but it is the essential element of the steel. This discussion did not at the time lead to a satisfactory conclusion. Quite recently Müller[3] has found nitrogen in not inconsiderable quantity in the gases extracted from Bessemer steel by boring, but thus far he has not been able to determine whether the nitrogen is simply enclosed in the pores of the steel or is chemically combined with it.

I have made a number of experiments with Bessemer steel and with other forms of iron, and have obtained results in accordance with those already on record. It seems possible that as regards steel the nitrogen detected may be partly absorbed from the air and partly present in combination with the iron, though it would be difficult to prove the correctness of this supposition.

May, 1881.

[1] Loc. cit. [2] Ibid. **19**, 409. [3] Berichte deutsch. chem. Gesell. **14**, 1.

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

[*Concluded from p.* 66.]

Materials employed in Washing.

Soap.—The consumption in the manufacture of soap of foreign fats, for the most part the product of hot countries, has very greatly increased, palm oil and coconut oil being of first-class importance, while to a less extent mafurra tallow, cotton-seed oil, peanut oil, and other such materials have been applied to this use. Large additional supplies of fat have come to be regularly obtained by extraction with carbon disulphide, and of late still better with light petroleum spirit, from the "marc" of olive pressing, from colza, cotton, and other seed cakes, from bones, slaughter-house refuse, cotton waste, etc., as has been noticed in a previous portion of this report, and these have in great measure fallen into the hands of the soap-boiler. In some respects, however, the most valuable of modern additions to his resources has been the "red oil" or crude oleic acid turned out in great quantity in pressing the solid fatty acids, palmitic and stearic, used in the manufacture of candles. The facility with which this free acid undergoes saponification, in comparison with the corresponding glyceride, is alone sufficient to distinguish it.

The chief feature in the supply of alkali has been the very general introduction of ready-made caustic soda, as contrasted with the old practice of causticizing the carbonate in the soap factory itself immediately before using it.

Of secondary materials introduced, a large proportion represent simply the fraudulent application of ingenuity in debasing the product with useless solid matter, or with water in excessive quantity, while preserving the appearance of good soap. Most of the so called "silicated" soaps, and those with which aluminum hydrate, potato starch and bone gelatine, with or without calcium phosphate, have been blended in quantity, are illustrations of this lowering of the standard of honest manufacture. The use of carnauba wax as the means of enabling soap to take up petroleum, while retaining the property of complete solubility in water, exhibits a curious case of modified behavior in relation to solvents. Some few of the additions made to ordinary soap for special uses have real value, as for instance the glycerine employed in the bland soap, made in great

perfection by Price's Patent Candle Co. for toilet use upon delicate skin, and the carbolic acid soap intended for medical and sanitary applications.

Greater care than was formerly common is given to the neutrality of soaps manufactured for industrial uses, as by bleachers, dyers, etc., avoiding excess either of alkali or of free fatty acid, particularly the former.

In the actual process of soap boiling, heating by means of steam has come more and more into use, replacing the use of open fires. The proposal to bring about saponification under increased pressure in close vessels, though sound in point of general principle, has not been practically applied on account of various inconveniences in detail which it involves. The most novel suggestion, that of Mr. Whitelaw in 1875, to make soap directly from common salt by heating together a neutral fat, excess of common salt, ammonia and water, raising the temperature to about 150°C. in a closed vessel, although it has not established itself in successful practical application, seems deserving of more careful study than apparently it has yet received.

Accessory Materials used in Washing.—In relation to Clark's process for softening water to be used in washing, it has been shown by experiments made upon the large scale that magnesia-hard water, containing magnesium carbonate dissolved by excess of carbonic acid, may be purified by means of calcium hydrate as completely and easily as water which owes its hardness to calcium carbonate. Clear lime-water proved much more satisfactory in producing precipitation than milk of lime, and from three to five hours sufficed for the settling of the precipitate, leaving the water clear.

Amongst alkaline materials adapted to increase the cleansing power of water, either with or without soap, the most useful which have been brought forward are borax and sodium silicate (soluble glass). The former has become generally available since California has furnished such an abundant supply, and borax soap is manufactured with which the salt is already incorporated. Soluble glass has been employed to some extent in the industrial preparation of new textile fabrics.

The addition of gum to the starch jelly used in giving stiffness to washed clothing has long been practiced with a view to improving the gloss of the surface, especially in order to render the appearance of new clothing attractive. There is some reason to believe that dextrine is substituted for natural gum, although such substitution does not seem to have been publicly noticed. If this be not practiced, it would be well that the efficacy of dextrine for this purpose should be tried, since it is obtainable of excellent color and at low price.

As the "blueing" intended to neutralize to the eye any yellowish tint remaining from imperfect washing or bleaching of cloth,

ultramarine and soluble Prussian blue have to a large extent taken the place of the indigo and smalt formerly in general use.

Of materials capable of rendering vegetable fabrics non-inflammable, retarding greatly their combustibility and preventing their ready ignition by contact with flame, sodium tungstate is best known, and has come into practical use upon a moderate scale. Other substances have however been employed with some success, and but recently a premium has been awarded by the French "Société d'Encouragement pour l'Industrie Nationale" for a mixture to be thus applied, consisting of ammonium sulphate 8 parts, ammonium carbonate 2, boracic acid 3, borax 2, and starch 2, to be dissolved in 100 parts of water.

Appendix to Washing.

Perfumes.—Many new perfumes of natural origin have from time to time been brought into public notice within the last few years, but a large proportion of these fail to establish themselves in permanent use. Among the more interesting and valuable of such materials may be mentioned: Champa or Champaca attur (*Michelia champaca*), from India; Grass oil (*Andropogon ivaracusa*), from India; Khuskhus oil (*Anatherum muricatum*), from India; Ylang-ylang oil (*Artabotrys odoratissima*), from Philippine Isles; Sampaguita attur (*gen. et sp. ?*), from Philippine Isles; Eucalyptus oils (*Eucalyptus*, of several species), from Australia; Myall wood (*Acacia pendula*), from New South Wales; Toronjil oil (*Cedronella Mexicana*), from Mexico; Lignaloes oil (*Amyris lignaloes*), from Mexico; Licoria wood (*Licoria odorata*), from Cayenne.

The chief novelties in regard to methods for the extraction of natural perfumes have been the substitution of paraffine for ordinary bland fats in the process of "*enfleurage*," thus avoiding the disagreeable consequences of the rancidity which the latter suffer sooner or later, and the employment of light petroleum spirit as an energetic solvent, which may readily be gotten rid of by evaporation at very low temperature, after it has served the purpose of extracting the delicate perfumes of such flowers as the violet, tuberose, jasmine, &c., which will not bear the temperature necessary for distillation with water. Other solvents of similar volatile character have been used; one of the last of these which has been proposed is methyl chloride, as made by Camille Vincent from the vinasse of beet-root molasses distillation.

The rapid progress of modern organic chemistry has contributed sundry artificial perfumes, although not in as great number and variety as the artificial dye-stuffs. Amongst the more prominent of such perfumes are "Mirbane essence," or nitrobenzene, simulating, though not perfectly, the odor of bitter almond; the real oil of bitter almonds, or benzoic aldehyde, identical in character and composition with the natural oil, but made from coal-tar toluene;

"Niobe essence," or methyl benzoate, artificially prepared with artificial benzoic acid; oil of winter-green, obtainable on a large scale and cheaply by means of Kolbe's synthetically made salicylic acid; artificial coumarine by Perkins' beautiful synthesis; and vanilline by the equally admirable process worked out by Tiemann and Haarmann.

Materials for Writing, Printing, &c.

Paper.—The most remarkable feature in the recent history of the manufacture of paper has been the substitution for rags to an enormous extent of a great variety of crude vegetable fibrous materials. Chief amongst these have been esparto grass[1] or "alfa" (a sedge from Spain and northern Africa), straw, maize leaves (with which excellent results have been obtained at Vienna), and soft wood of various trees. Bamboo[2] and sugar-cane or sorghum "*bagasse*," although affording coarse fibre, admit of being successfully used, and are obtainable in immense quantity; they have not as yet been actually employed to any great extent. Short, weak fibre, fit mainly to be worked up along with other and better material, has been obtained from pressed beet-root pulp of the sugar factories, cotton-seed hulls, and a great number of other sources.

The employment of these materials, in which the pure vegetable fibre is incrusted and cemented together by other substances, has demanded the general application of a disintegrating process, consisting in heating with alkaline lye, often under a pressure of 3 or 4 atmospheres in close vessels. The use of the acid sulphite of sodium or calcium instead of caustic soda for this purpose has recently been patented by Mitscherlich, and it is claimed that the substitution produces fibre much superior in length, strength and whiteness to that yielded by the older process, bleaching with chloride of lime being rendered unnecessary or reduced to a minimum.

There have been sundry improvements in pulping engines, in the details of the bleaching process, and in the paper-making machinery proper, but these either involve no changes of radical importance, or belong to the domain of the mechanical engineer rather than the chemist.

In getting rid of the residual chlorine after bleaching, the tendency has for some years been in the direction of using "antichlors" more sparingly, but washing more thoroughly. It is asserted that editions of books issued during the period when sulphites and thiosulphates were most freely employed as antichlors show manifest signs of more rapid deterioration of the paper

[1] As evidence of the eagerness with which any new fibre really fit for paper-makers' use is seized upon, it may be mentioned that England imported of esparto: In 1860, less than 1000 tons; in 1865, more than 50,000 tons; in 1871, 140,000 tons.

[2] Bamboo fibre has long been used in China, and, to a less extent, in Japan.

than either those of the last few years or those of the period before chlorine bleaching was practiced. The liberation of free sulphur in a state of extreme subdivision from sodium thiosulphate (old hyposulphite) constitutes a special objection to it. It has been proposed to use in preference to these salts a very weak solution of ammonia.

The theory of resin-sizing of paper has been not long since carefully examined by Wurster and Conradin, and the most advantageous conditions studied for precipitating smoothly and in a very fine state of division the free acids of the resin soap by means of aluminum sulphate. The same chemists advocate the precipitation in the pulp of barium sulphate by the reaction of barium chloride on the sodium sulphate formed in the precipitation of the resin soap. The addition of a little glycerine in connection with the sizing has been found to give a special softness and pliability to the paper.

Of special modifications of paper introduced in comparatively recent times, the most valuable is "parchment paper," made by immersion for a short time in sulphuric acid diluted to 59° or 60° B., and kept at a temperature not higher than 10° or 12° C. By using paper from mixed fibres, as of linen and cotton, which are acted upon with unequal rapidity, and by limiting the extent to which the change is allowed to penetrate beneath the surface of thick paper, products combining horny hardness with flexibility in various different degrees are manufactured. The thin, delicate Japanese paper (chiefly from Kodzu, *Broussonetia papyrifera*, and Kuwa, *Morus alba*), intended for transient use in the form of napkins, handkerchiefs, curtains, etc., and the Japanese waterproof paper in imitation of leather, prepared by treatment with successive coats of a drying oil, have both been reproduced in western hands with a fair degree of success, though not as yet upon a very large scale. An "incombustible" paper has lately been described as made in France by mixing 2 parts of paper pulp with 1 part of asbestus, soaking the mass with a solution of alum and common salt, making into paper on the ordinary form of machine, treating the surface with a solution of shellac, passing between rollers and cutting into sheets. It is said that if this paper be written upon with common ink (from nut-galls and copperas), the paper and writing are not destroyed by exposure to fire, *i. e.* doubtless, not so far destroyed as to prevent the possibility of deciphering the writing. At the time of the great Boston fire a few years ago, it was observed that heavily "clayed" paper most resisted destruction, while pencil marks were more generally found legible than those made with ink.

Ink.—The chief novelty in the manufacture of writing ink has been the introduction of various colored inks—particularly violet; to a less extent red, blue and green—prepared with solutions of the coal-tar colors. These have the advantage of flowing freely from the pen and drying quickly, but they are deficient in dura-

bility, being easily destroyed in greater or less degree by light, heat and age. The best is doubtless that made from soluble aniline black, which material can readily be carried about in the dry state and dissolved in a few moments for use, thus representing the most convenient form of "portable ink." The comparatively moderate price at which vanadium compounds can now be had admits of the revival of Berzelius' suggestion of half a century ago, to use as ink the very dark colored fluid obtained by mixing ammonium vanadate solution with infusion of nut-galls; the product was highly recommended by him on the score of color, fluidity and indelibility. Amongst somewhat recent modifications of common writing ink from galls and copperas may be mentioned the addition of salicylic acid as a preventative of moulding, and the use of glycerine in copying ink to prevent rapid drying of the writing.

Amongst new materials for the manufacture of printing ink also, the coal-tar colors have played a principal part. Brilliant effects have been cheaply obtained by means of them. The most interesting form in which they have been applied is that of fatty acid compounds of the color bases, readily miscible with linseed oil, and well adapted to the production of inks for chromo-lithography. In the preparation of the higher grades of ordinary black printing ink there has been no more important improvement than the introduction of the very fine lamp-black, so-called "Diamond black," made by the smothered combustion of natural hydrocarbon gas (chiefly methane) in the petroleum region of Ohio. The purity of the carbon so obtained, its extremely fine subdivision, smoothness, and intense jetty black appearance, render it fit for the production of the very best printing and lithographic ink.

As "indelible" ink for marking clothing, carbon inks of the same general character as those used by printers have come largely into use in the United States instead of the nitrate of silver preparations; but the most valuable novelty in this direction has been the "Jetoline" brought forward a few years ago, intended to develope insoluble aniline black upon the cloth to be marked, by writing with a mixture, prepared in small quantity immediately beforehand, of the two liquids furnished, one of these being a solution of an aniline salt and the other one of a vanadium compound, with the necessary amount of potassium chlorate or other oxidizing agent.

Mucilage.—For mucilage to be used in uniting surfaces of paper, the cheap and nearly colorless dextrine of modern manufacture, and "liquid glues" made from gelatine with a small addition of nitric, hydrochloric or acetic acid, or of alum, aluminum sulphate or zinc sulphate, have largely replaced the natural gums. To prevent fermentative change in this, as in so many other organic liquids, salicylic acid has been found to answer a useful purpose. It has been ingeniously proposed to apply the insolubility of chromated gelatine after exposure to light for sealing letter envelopes in such a way that they can only be opened by tearing or cutting the paper.

The part of the envelope to be covered by the flap, and which is not touched by the lips or tongue, is coated with a preparation consisting essentially of acid ammonium chromate, copper and ammonium sulphate, and a little fine white paper fibre, while the inside of the flap is coated with isinglass gelatine dissolved with the aid of acetic acid. When the envelope has been closed, the two prepared surfaces are after a short time united so as to resist the action of cold or hot water, steam, and weak acid or alkaline solutions. The same material, chromated gelatine, has been employed as a varnish to render paper water-proof. In a different direction gelatine has been made available for writing purposes, by converting a mixture of its strong solution with glycerine into the simple and useful tablets which, under various names, such as "hectograph," "polygraph," etc., have been applied to the reproduction in numerous copies of letters and other ordinary writings in aniline ink.

Artists' pigments.—To the list of the fine pigments employed by artists there are frequently made additions, but the number of new and really valuable materials under this head is quite small. Probably the most important for some years have been artificial ultramarine of various tints, Guignet's bright chrome green (chromic oxide,) and cadmium yellow (sulphide of cadmium). The aniline colors, in the form of lakes, have furnished a number of bright effects, but these blend but poorly to delicate mixed tints, and are sadly wanting in permanence on exposure to light. This latter defect constitutes a grave objection to the use of the vivid "iodine scarlet" (mercuric iodide). Uranium yellow (chiefly sodium uranate) has been a little used as an ordinary pigment, but serves mainly the purposes of glass staining and decorating porcelain. Of other colors which have more or less come into use of late years may be noticed cobalt yellow (Fischer's salt—cobalt and potassium nitrite), light or lemon chrome yellow (barium chromate), Indian yellow (Purrée—magnesium euxanthate—long known in the East, but of still very uncertain origin), Cassel green (barium manganate), Arnaudon's and Matthieu-Plessy's greens (chromium phosphates), tungsten greens (copper and chromium tungstates), tungsten blue (tungsten pentoxide), tungsten white (barium tungstate), and copper brown (cupric ferro-cyanide). None of these, however, can be considered as additions of first-class importance to the list of well established pigments.

J. W. Mallet.

Recent Progress in Agricultural Science.

[*Continued from Vol. 2, p. 432.*]

Respiration.—That plants, like animals, take up oxygen from the air, to exhale it again in combination with carbon and hydrogen, is a fact which has long been known. The reverse process of the reduction of carbonic acid by the green parts of plants is, however, a much more striking and apparently characteristic function of vege-

tation, so that it has come to pass that the first-named process has been comparatively little studied, and the second has not infrequently been called the respiration of plants, thus tending to convey the notion of a fundamental difference between plants and animals as regards their relations to the oxygen of the atmosphere. More recently, however, greater accuracy of nomenclature has prevailed, the absorption of carbonic acid and exhalation of oxygen being designated as assimilation, while the term respiration is applied to the process which is identical in its general character in plants and animals and which is essential to all life, viz. the taking up of oxygen and its use in the organism to oxidize complex substances and liberate the latent energy which they contain.

The clear recognition of the importance of the respiratory function in plants has led to numerous investigations which have disclosed some interesting results. According to the views described in a previous article, the respiration of plants is closely connected with their proteid metastasis and is a function of the protoplasm of the living cells. This view appears *a priori* very probable, since all vital activities are manifested through protoplasm, and is supported by analogy with the respiratory process in animals, where, we believe, the decomposition of matter in the cells of the body is the primary process, while the oxygen which is taken up unites with the products of this decomposition. The observations of Corenwinder also favor this view. He found[1] that respiration, as measured by the amount of carbonic acid given off, was much more active in young parts of plants, rich in protoplasm, than in those older parts in which the proportion of protoplasm was much less. Freyberg[2] has made similar observations. He executed comparative respiration experiments on land and marsh plants, measuring the amount of oxygen taken up, and found that the former showed a much greater intensity of respiration, while analysis showed them to be also richer in nitrogenous compounds. On this fact, in connection with the greater supply of air to the interior of aquatic plants through their air-ducts, he bases the explanation of the fact that the roots of these plants thrive in a soil nearly or quite destitute of oxygen. Even among land plants the rate of respiration was found to follow pretty closely the percentage of nitrogen in the dry substance.

Internal Respiration.—As just stated, respiration proper is thought to consist in the oxidation of the products resulting from the splitting up of the nitrogenous matters of the protoplasm. This splitting up itself is believed to take place independently of oxygen, and frequently it goes on in the absence of this element. One of the products of this action is usually, if not always, carbonic acid, which under proper conditions is exhaled, and this process is generally called internal respiration. The action of yeast, and especially its so-called "self-fermentation," furnishes a good ex-

[1] Jahresber. Agr. Chem. N. F. 1, 312.

[2] Landw. Versuchs-Stationen, 23, 62.

ample of internal respiration. The force necessary to sustain the life of the plant is produced solely by the splitting up of the materials of the cell, and not partly by oxidation as is normally the case in the higher plants. Other fungi behave similarly. Müntz,[1] in observations on *Agaricus campestris*, confirmed in the main the results of previous investigators, and showed that this fungus in the presence of oxygen took up this gas and exhaled carbonic acid, while in the absence of oxygen the exhalation of carbonic acid still continued and alcohol was formed in the plant.

A similar process takes place also in the higher plants. Böhm[2] has found that when green leaves are placed in a limited volume of an indifferent gas in the dark, the volume of the gas increases, carbonic acid being formed in the leaves by internal respiration and excreted. When the same apparatus was exposed to sufficiently strong light, no change in the volume of the gas took place, the carbonic acid being decomposed again as soon as formed, while the oxygen liberated was applied to sustain normal respiration. So too it was found that when green leaves were placed in a mixture of hydrogen and nitrogen containing 6 to 10 per cent. of carbonic acid and exposed to the sunlight, the volume of oxygen given off was greater than that of the carbonic acid assimilated, and that the difference was more marked the longer the apparatus remained in the dark after being put together. This excess of oxygen came from the reduction of the carbonic acid formed by internal respiration. Déhérain and Maissan[3] have also observed that green leaves continue to excrete carbonic acid in an atmosphere free from oxygen.

In Böhm's experiments leaves of *Juglans regia* were chiefly employed, and these organs were found to be very sensitive to the presence of oxygen, the smallest trace of this gas in the surrounding atmosphere being sufficient to suspend the internal respiration. Further experiments showed that this was not always the case. When green twigs of woody plants were placed in air or oxygen over mercury in the dark, a diminution of the volume of the gas at first took place, which was attributed either to a chemical retention of oxygen by the organic matter of the twig or to a mechanical retention of the carbonic acid formed in respiration. Before, however, all the oxygen was consumed the volume of the gas began to increase, carbonic acid being formed by internal respiration and exhaled. With slender twigs this only took place when all but a trace of the free oxygen had disappeared, but with thicker twigs it began in an atmosphere which still contained several per cent. of oxygen. The cause of this phenomenon is evidently that the air as it diffuses into the twig is gradually robbed of its oxygen, so that the central cells receive none, and thus exhibit internal respiration while the surrounding air still contains a considerable quantity of oxygen.

[1] Jahresber. Agr. Chem. **18–19**, 1, 400. [2] Liebig's Annalen, **185**, 248.
[3] Jahresber. Agr. Chem. **16–17**, 1, 273.

The internal respiration of such green twigs may also be rendered evident by immersing them in boiled water and exposing them to sunlight, as was done by Böhm. Treated in this way in the dark, they turned brown in two or three days and entered into butyric fermentation, but in direct sunlight they mostly remained fresh for a week or more and evolved considerable gas (sometimes more than their own volume), consisting chiefly of oxygen. This oxygen was evidently derived from the carbonic acid produced by internal respiration.

This evolution of oxygen by green parts of plants under boiled water in sunlight is, as Böhm himself points out, not a new fact. It was observed by De Saussure in experiments on *Cactus opuntia*, but the cause of the phenomenon was quite different in this case. These plants have the power of absorbing their own bulk or even more of carbonic acid in the dark, and when afterwards exposed to the light set free a corresponding amount of oxygen. De Saussure also observed frequently an evolution of carbonic acid by plants placed in oxygen-free media, but considered it a product of decay, holding that no life was possible in the absence of oxygen. It thus appears that Böhm's results of themselves are not new, but differ from the old ones of De Saussure only in the interpretation given them.

It should likewise be mentioned that Ad. Mayer has observed a similar evolution of oxygen by certain *Crassulaceae*, which was due to the reduction of organic acids in the plant, and that he suggests the possibility of a similar interpretation of Böhm's experiments.

Normal Respiration.—Commonly, when we speak of the respiration of plants, we mean the respiration which is sustained by the oxygen of the external air, and this respiration we may designate as normal or external respiration to distinguish it from the internal respiration just spoken of.

Several recent investigations have had it for their object to ascertain the relations of normal respiration to the temperature and to growth. Among the earliest of these is that of v. Wolkoff and Ad. Mayer.[1] They experimented on germinating seeds, chiefly of *Vicia faba* and *Tropaeolum majus*, in an apparatus devised by them, which permitted a very exact measurement of the amount of oxygen taken up from a confined volume of air. Preliminary trials showed that under uniform conditions the respiration remained constant for several hours, and that the pressure of the air in the apparatus and the percentage of oxygen which it contained had, within quite wide limits, scarcely any effect on the rate of the respiration. It was also found that while changes of temperature affected the rate of the respiration, the latter promptly returned to its original amount when the original temperature was restored. Several series of experiments were then made to determine the influence of temperature on respiration. For temperatures ranging

[1] Landw. Jahrb. 3, 481.

from 16° C. to 35° C. the intensity of the respiration (*i. e.* the quantity of oxygen taken up in a unit of time) was found to be directly proportional to the temperature reckoned from the freezing point of water. Above 35° the plants began to suffer from the high temperature, the tips of the stems appearing flaccid and translucent like frozen or boiled tissue. Exactly these parts, now, are the seat of rapid growth and consequently of rapid respiration, and as a natural consequence the intensity of the respiration was found to diminish at these high temperatures. The authors believe, however, that the respiration of the uninjured parts of the plants continued to increase with the temperature, though not so rapidly as below 35°. At any rate, these results indicate that the optimum temperature for the respiration of these plants is quite high, and considerably higher than the optimum temperature for the growth of most plants which have been examined in this respect.

Experiments were also made upon the influence of light on respiration. As is well known, the effect of light on growing plants is to decrease the growth in length. This effect might be explained very plausibly by the supposition that the light increases the oxidation of the substance of the plant and thus diminishes the supply of matter for the formation of new tissue, but these experiments showed very decidedly that sunlight had certainly only a very slight influence, and most probably none at all, upon the rate of respiration.

These two series of carefully conducted experiments are valuable for the facts they have brought to light regarding the relations of respiration to temperature and illumination, but they are even more valuable because they show that while growth and respiration are more or less related processes, they are not so intimately connected that the amount of one can be inferred from that of the other.

Schützenberger and Quinquand, and also Déhérain and Maissan, have likewise observed that the respiration of plants proceeds at the same rate in darkness and in light.[1]

Ad. Mayer[2] has also investigated the respiration of germinating wheat by means of the apparatus devised by him in conjunction with v. Wolkoff. The results were controlled by determinations of the loss of dry matter suffered by the seedlings, it being assumed that the substances destroyed in respiration had the composition of starch. The results obtained in these two ways were fairly accordant. In the later stages of growth, when the plants became too large to be contained in the respiration apparatus, the second method alone was employed.

The wheat used was all from the same crop and of very nearly uniform weight, each grain weighing 0.05 gram. After soaking for a suitable time, it was allowed to germinate in the dark, and the rate of respiration, *i. e.* the amount of oxygen consumed per day, the daily growth in length, and the loss of dry matter were determined.

[1] Jahresber. Agr. Chem. **16-17**, 1, 273. [2] Landw. Versuchs-Stationen, **18**, 245.

Three series of experiments were made, at temperatures of 11.8°, 23.8°, and 34° C. In each case the rate of respiration was found to increase rapidly at first, to reach a maximum after a certain time, and, after remaining nearly constant for a short time, to again decrease as the supply of organic matter from the seed became exhausted. A comparison of the results obtained at different temperatures showed, as was to be expected, that at high temperatures the maximum rate of respiration was higher and was reached more quickly than at low temperatures, while the decrease after the maximum was passed was equally rapid. The same amount of organic matter which was oxidized in 34 days at 11.8° C., was oxidized in about 16 days at 23.8° C., and in 10 days at 34° C.

As regards the relations between respiration and growth (as expressed by the increase in the length of the plumule), it was found in the first two series that the rate of growth corresponded pretty closely with the rate of respiration, though the former reached its maximum a little later than the latter. In the third series only the loss of dry matter was determined, and this was found not to furnish sufficiently accurate data for a similar comparison. An interesting result was reached by comparing the total amount of organic matter oxidized in the three cases with the total amount of growth.

	Days from beginning of experiment.	Loss of dry matter by 4 seedlings.	Length of plumule.	Length of longest root.
I.	34	0.090 gram	222 mm.	49 mm.
II.	16	0.089 "	252 "	111 "
III.	10	0.090 "	147 "	106 "

A direct comparison like this of plants from different series of experiments is somewhat uncertain, and the results are rather irregular. Nevertheless it is evident that the oxidation of the same amount of dry matter produced decidedly less growth of the plumule in the experiment carried on at a temperature decidedly above the optimum for growth. Mayer therefore concludes that at high temperatures part of the organic matter of the plant is oxidized without producing any visible effect on its growth. This result evidently points in the same direction as those already adduced, and shows that growth and respiration are not strictly parallel processes. In another investigation, supplementary to the preceding, Mayer[1] has shown by means of respiration experiments executed on the same plants, that the intensity of the respiration is directly proportional to the temperature, beginning nearly at 0° C. and increasing regularly up to about 40° C. According to Sachs the temperature of most rapid growth for the wheat plant is about 29° C., so that we have here another proof of the partial independence of growth and respiration.

As noted, Mayer determined the amount of oxygen taken up by his plants. Rischawi has made experiments similar to Mayer's,

[8] Landw. Versuchs-Stationen, **19**, 340.

but used an apparatus which enabled him to collect and weigh the carbonic acid given off by a large number of plants, and which made it also possible to continue the experiment with the same plants as long as was desirable. His results on wheat fully confirm Mayer's. Experiments on beans gave quite a different result. It was found that for nearly three weeks the rate of respiration remained practically constant, a result which is evidently connected with the large stock of reserve matters contained in these seeds, and which Rischawi explains by supposing that the cotyledons at first respire vigorously, and that as the young plant begins to respire more and more the respiration of the cotyledons becomes gradually less energetic.

Rischawi also utilized this constancy of the respiration of the bean in experiments on respiration in pure oxygen. The receiver of his apparatus was filled with young bean plants and connected with gasometers from which either air or oxygen could be supplied at pleasure. The amount of carbonic acid excreted was determined every hour, the apparatus being filled with air for the first hour, oxygen for the second hour, and so on alternately. These amounts were found to be sensibly equal whether the respiration took place in air or oxygen. The experiments were executed at temperatures ranging from 2° C. to 30° C. with the same result.

In the first of these reports[1] mention was made of experiments by Böhm and by Bert, showing that growth cannot take place in pure oxygen at the ordinary pressure. Böhm found that the amount of oxygen taken up under these circumstances was the same as when the seeds were exposed to atmospheric air, while Bert found it to be less. Rischawi's results evidently confirm Böhm's, while they perhaps give another indication of the non-parallelism between growth and respiration.

H. P. ARMSBY.

NOTES.

Asbestos Stopper for Combustion Tubes.

Some years ago, when working in the laboratory of organic chemistry of Harvard University, I conceived the idea of an asbestos stopper for combustion tubes, which I make as follows: The asbestos is separated into fine threads, moistened with water, twisted into a plug, crowded into the cylinder of an ordinary steel crusher, such as is used to pulverize minerals for analysis, and compressed

[1] This Journal, 2, 342.

by driving the piston of the crusher down upon it with a hammer, or better, by the screw of a vice. The plug is kept under pressure for several hours, then dried within the cylinder upon a sand-bath, pushed out of the cylinder, and after ignition over a blast-lamp is ready for use.

In this condition the plug loses no weight under prolonged ignition, is elastic enough to make a tight joint when fitted to a combustion tube of suitable size, and may be smoothly perforated with an ordinary cork borer.

Besides simplifying the method of organic analysis by permitting the substitution of short metallic tubes for the long glass combustion tubes in ordinary use, asbestos stoppers are very useful for closing bottles which contain substances corrosive to stoppers of rubber or cork.

J. Fleming White,
Laboratory of U. S. Geological Survey.
Newport, R. I., April 20, 1881.

Action of Ozone on Germs contained in the Air.

E. Chappuis has attempted to show that ozone has the power to destroy the germs which are the cause of fermentation and other similar phenomena. For this purpose dust from the air was collected on cotton stoppers, and some of these exposed to the action of ozone. The ozonized stoppers were then brought in contact with liquid beer yeast, the necessary precautions being taken to prevent the introduction of other material. Even in twenty days no effect was produced in the clear liquid, while the unozonized stoppers caused turbidity even in a few days from the development of certain organisms. Hence ozone kills the germs in the air which can develop in beer yeast. Extended experiments may show whether there exist any relations between the sanitary condition of a place and the amount of ozone in the air, as according to modern views the spread of contagious diseases is caused by germs or low organisms which are transported by the air.—(*Bull. Soc. Chim.* 35, 290.)

The Quinquivalence of Boron.

Not long since, Councler announced the preparation of an oxychloride of boron of the formula $BOCl_3$, analogous to the oxychloride of phosphorus. The existence of this compound indicates the quinquivalence of boron. Michaelis and Becker have attempted to make the oxychloride by a simpler method than that employed by Councler. They first passed ozone into the chloride ; then they exposed a mixture of oxygen and the chloride in the form of vapor to the action of the silent discharge of a very strong induction coil ; and finally they passed electric sparks for a length of time through a mixture of oxygen and boron chloride. They were unable, however, to obtain even a trace of the oxychloride.—(*Ber. deutsch. chem. Gesell.* 14, 914.)

Evaporation without Fusion.

Lothar Meyer has repeated the now well-known experiment of Carnelly which seemed to indicate that ice could be heated to a temperature much above 0° without undergoing fusion, and comes to the conclusion that the ice has not really a temperature above 0°. As regards the form of apparatus and the details of the experiment, reference can only be made to the original article.—(*Ber. deutsch. chem. Gesell.* 14, 718.)

On the Absorption of Solar Rays by Atmospheric Ozone.

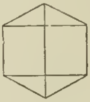
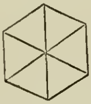
W. N. Hartley has been engaged for some time past in studying the absorptive effect produced by ozone on sun light. He has shown that columns of air only three feet in length, containing only $\frac{1}{2000}$ of their volume of ozone, cause a most energetic absorption of the invisible rays, and he has further found that very small quantities of the gas give an azure-blue tint to very considerable volumes of air. He says: "Messrs. Hautefeuille and Chappuis discovered the fact that the ozone possessed a blue color. On filling a glass tube two feet in length for the purpose of some of the preceding experiments, I was surprised to find how small a proportion of ozone is visible to the eye."

"In a column of the atmosphere 1 square centimeter in sectional area, which would weigh 1033.33 grams, the maximum amount of ozone would be at least 0.00258 gram, supposing the gaseous constituents of the atmosphere to form a homogeneous mixture. This calculation is based on the determination of the amount of ozone in the air made by M. Houzeau. The proportion by weight at the *maximum* was $\frac{1}{450000}$, or by volume $\frac{1}{700000}$. In a 2 foot tube a full pure sky-blue tint is seen when 0.002542 gram of ozone is contained in each square centimeter of sectional area. This number approximates very closely to the above, hence it is evident that if these determinations be correct, the blue tint of the atmosphere must certainly be due to some extent to ozone, at times if not always."

"Now if we consider that 2.5 mgrms. of ozone in each square centimeter of sectional area of a column of air produce a full sky-blue tint, it is impossible to believe that light, which has traversed columns of air under ordinary conditions of temperature and pressure, and 27 to 35 miles in length, has not made its way through 2.5 mgrms. of ozone. The length of an atmospheric column at the ordinary temperature and pressure would be 5¼ miles, and while we are in doubt as to the constitution of the higher atmosphere, such reasoning cannot justly be applied to the blue color of the sky."—(*Jour. Chem. Soc., March*, 1881, 111.)

On Carboxytartronic Acid and the Structural Formula of Benzene.

About two years ago, in Barth's laboratory, M. Gruber, by treating protocatechuic acid with nitrous anhydride, obtained an acid of the formula $C_4H_4O_7$, which was called carboxytartronic acid. The acid is tribasic, and hence, according to commonly accepted notions, must consist of three carboxyl and one hydroxyl group united with one carbon atom. Accepting the common benzene formula, it is difficult to explain how an acid of the formula described can be formed from protocatechuic acid without assuming that the carboxyl is not split off, and this assumption seems improbable. BARTH has now succeeded in obtaining the carboxytartronic acid from pyrocatechin, thus proving that the carboxyl of the protocatechuic has nothing to do with the formation first mentioned. The result also makes it appear extremely probable that in benzene four carbon atoms are in combination with each other. As is well known, however, the commonly accepted formula does not represent this condition in benzene, whereas either the prism formula or the "star" is in harmony with the fact recorded by Barth. These formulas may conveniently be represented respectively thus:

 and 

It will be remembered that the recent investigations of Thomsen on the thermal phenomena presented by benzene led him to the conviction that one of the above formulas is correct.—(*Monatshefte f. Chemie,* 1, 869.)

On the Conduct of Palladium, Rhodium and Platinum towards Illuminating Gas.

THEODOR WILM has found that, when the double salt of palladium chloride and ammonium chloride is decomposed carefully in a small porcelain crucible over an ordinary Bunsen burner, and the residue ignited after all the ammonium chloride has escaped, the metal turns a copper color and black, while black rings and spots are formed around it, which creep up the inner walls of the crucible, covering it more and more; and, if the crucible be ignited with the cover loosely laid on, there is formed between the cover and the upper edge of the crucible a cauliflower-like growth of carbon. This carbon is not burned up by further ignition even in an open crucible. This phenomenon has nothing to do with the

formation of a compound of palladium and carbon, but consists simply in a decomposition of illuminating gas by the metal and a separation of carbon, which, however, is deposited mostly on the crucible in the neighborhood of the metal, but not on the metal itself. Rhodium conducts itself quite differently. Only a trace of carbon is deposited on the crucible, but the metal itself is markedly changed, a compound with carbon being apparently formed. Platinum conducts itself unlike either of the two metals mentioned. Like palladium it sets free the carbon of illuminating gas by simple contact, but the carbon is then deposited in the pores of the metal and does not enter into combination with it. It appears from these observations that the presence of palladium and rhodium in platinum vessels is objectionable. Platinum crucibles into the composition of which these metals enter soon become blistered or perforated; while vessels of pure platinum do not suffer from long continued use.—(*Ber. deutsch. chem. Gesell.* 14, 874.)

On the Atomic Weight of Platinum.

K. Seubert has made a careful determination of the atomic weight of platinum, and finds it to be 194.46. According to the "periodic law" the atomic weight of platinum should be less than that of gold (Au=196.2), whereas hitherto it has been commonly accepted as greater. Platinum now takes that place in the series Ir < Pt < Au which would naturally be accorded to it if its properties be taken into consideration.—(*Annalen der Chemie*, 207, 1.)

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Davison, J. Aids to the Chemistry and the Tests of the Pharmacopoeia. Dublin: Fannin. 1s. 6d.

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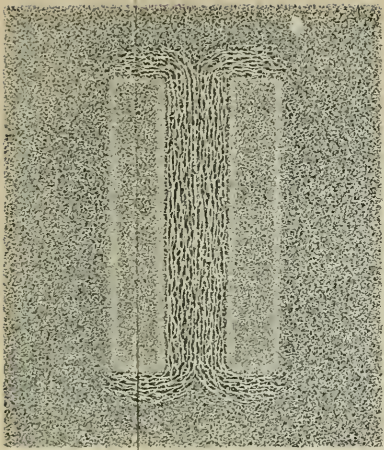

Fig. 1.

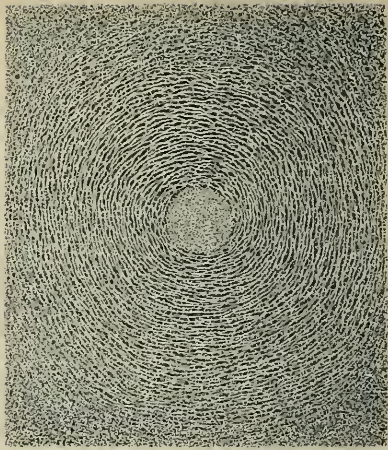

Fig. 4.

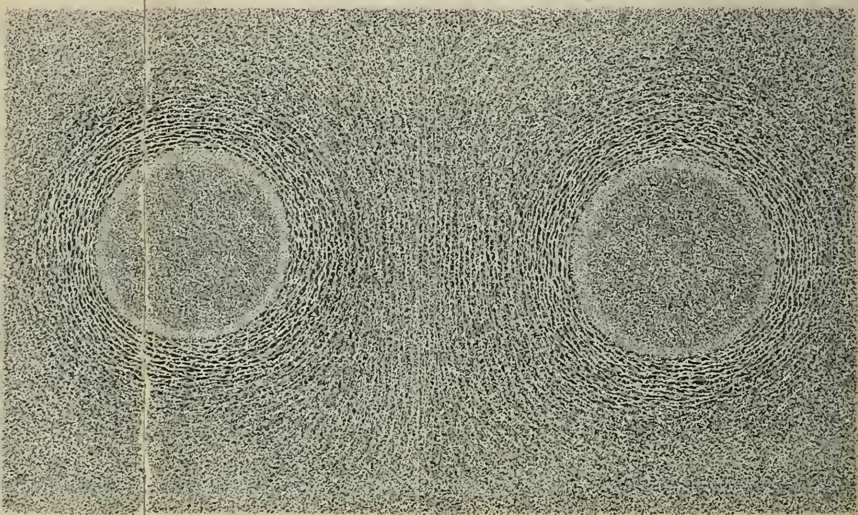

Fig. 2.

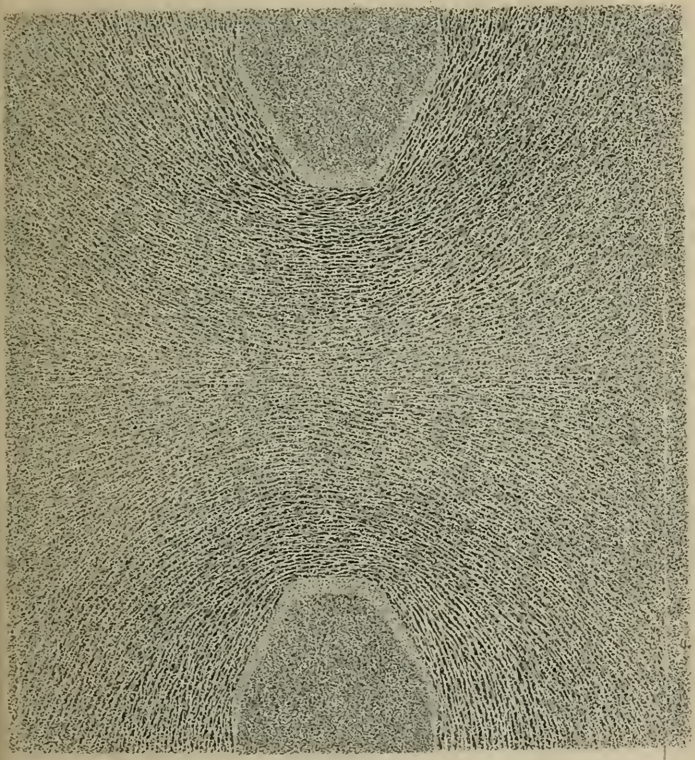

Fig. 3.

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AMERICAN CHEMICAL JOURNAL.

CHEMICAL ACTION IN A MAGNETIC FIELD.

By Ira Remsen.

I.—*On the Deposition of Copper on Iron in a Magnetic Field.*

The question whether a metal in the magnetized condition differs in its chemical conduct from the same metal unmagnetized seems to be a fair one to ask, but, on first thought, the chances appear to be very much against obtaining a satisfactory answer. A difference in the *intensity* of the action of the metal in the two conditions would naturally be looked for first; but how can such a difference be detected in ordinary cases? Take the action of hydrochloric acid on iron for example. If a piece of iron be magnetized and treated with the acid, and the amount dissolved in a given time compared with the amount of a similar piece of unmagnetized iron dissolved under exactly the same circumstances, perhaps a difference might be detected. But the conditions are very complex, and it would be difficult to draw conclusions from experiments of this kind, particularly as the differences with which we would have to deal would probably be very minute. It is, further, possible that the total chemical action which takes place between hydrochloric acid and a piece of magnetized iron, on the one hand, and that which takes place between the same acid and a piece of unmagnetized

iron on the other, may be identical, while, at the same time, the action may be distributed differently in the two cases—in the one case taking place uniformly and in the other irregularly, being more intense in some places and less so in others. If this latter view be correct, and *a priori* it seems probable, then it should be possible to detect evidence of the influence of magnetism on chemical action. Taking again the case of iron and hydrochloric acid, if the action is irregular, then, after it has continued for some time, the iron itself should present the evidence of this fact in an irregularity of surface. Figures of some kind should be etched on the iron, and these would indicate the distribution of the action, as they would, of course, be deepest where the action is strongest, and, in general, the depth of the marks would be approximately proportional to the intensity of the chemical action.

Reasoning somewhat in the above manner, I was led a short time ago to undertake some experiments, the results of which are recorded in this paper. I have succeeded in showing, by means of a very simple experiment which any one may repeat in a short time, that magnetism does, in some way, as yet not understood, influence certain kinds of chemical action very markedly. Up to the present the experiments have been confined mainly to one particular case, that of the deposition of copper on magnetized iron. The results already reached in this case are so surprising and interesting that it appears to be desirable to put them on record at once, without waiting to take up other cases which will readily suggest themselves.

Experiments were first made on the action of dilute hydrochloric acid on thin iron sheets placed in thin glass vessels over the poles of magnets, but no satisfactory results were obtained. The iron used was as good thin sheet iron as I could get, but was very irregular in structure, and, if the magnetic condition of the iron had any influence on the action of the acid, the effects of this influence were so completely disguised by the structure of the iron as to escape detection. I have not yet given up the hope of obtaining results in this direction, but, in the meantime, a simpler method led unexpectedly to success, and I have temporarily abandoned the first line of experiments.

A shallow vessel of thin iron containing a solution of copper sulphate was placed on the poles of a permanent magnet of Jamin's construction capable of supporting twenty-five kilograms. In the course of one or two minutes the outlines of the poles could be

clearly seen through the solution. On pouring off the solution after allowing the action to continue for a time, the only result that could be seen was this: The copper was deposited in a fairly uniform way on the entire plate, except at the lines marking the outlines of the poles. These lines were sharply marked as depressions in the deposit, thus indicating that less action had taken place there. This experiment was repeated a number of times, the conditions being improved as much as possible. The only additional result obtained with the permanent magnet used was the development of lines other than those marking the poles, and much less regular. Between the poles, which are rectangular in shape, interrupted lines appeared parallel with the sides of the poles which were directed towards each other. These lines were produced by irregularities in the deposit of the copper. They appeared not only in the space between the poles, but at the ends of this space they curved outwards, and could be followed to the outer edges of the poles, and there showed a tendency to run parallel to those between the poles. The direction of these lines is shown in the accompanying lithographic plate Fig. 1. It will be seen that in general the direction is at right angles to the lines of force.

The result described naturally led to the inquiry whether, with a different shape and arrangement of the poles of the magnet, the copper would be deposited in similar irregular ridges at right angles to the lines of force, and a number of experiments have been performed to decide this point. First, a small electro-magnet with cylindrical poles 7 inches long by 1 inch in diameter and separated about 3 inches, was used. It was connected with a Bunsen dip-battery of six cells, such as is commonly used in chemical laboratories. The iron vessel and the copper sulphate solution were the same as those used in the experiments with the permanent magnet. The action in this case was very striking. Within half a minute the outlines of the poles were clearly visible. A space of about one sixteenth of an inch in width followed the circular form of each pole, and, as in the case first described, the development of this space was due to the fact that here no copper, or very little at least, was deposited, leaving the smooth surface of the iron practically in its original condition. On the parts of the iron included within these circles, that is, directly over the poles, there was a fairly uniform deposit. Outside of the circles, however, the most surprising effects were produced. The greatest amount of deposit was immediately adjoining the blank circles above referred to. From these places the copper

was deposited in irregular ridges, the general direction of which it was impossible to mistake. The ridges grew less and less distinct from the poles outward, and were finally lost, in the case under consideration, at about one and a half inches from the poles. These ridges are, as nearly as could be determined, at right angles to the lines of force, and consequently, *coincident with the lines marking the equipotential surfaces.* These ridges are not indistinct and difficult to recognize, but are very marked and their direction is unmistakable. An approximate representation of the appearance of one of the iron plates used in these experiments is given in Fig. 2, but the beauty of the phenomenon cannot be described nor represented.

A third form of the experiment was now tried. A large electro-magnet, connected with a battery of twelve Bunsen's cells arranged in series, was used. The construction of the magnet is such that the poles are in the same line and the distance between them can be changed at will. The usual vessel with the solution of copper sulphate was placed in position on the poles, which were separated about two inches. Almost instantly the sharply defined outlines of the poles became visible, not a particle of copper being deposited upon these lines. Directly over the poles the deposit was nearly uniform as in the previous cases. Arranged over the whole plate except the portions just mentioned were again the remarkable ridges of copper, the direction of which changed gradually in passing from the edges of the plate nearest the poles towards the centre. At first they conformed nearly to the shape of the poles, but they became less and less curved the farther they were removed, until midway between the poles they were straight and at right angles to the line joining the poles. These lines were clearly developed within a minute from the time the action began, and could be seen distinctly through the solution. On first pouring off the solution the plate presented an appearance of striking beauty, the strongly marked ridges having the pure copper color, and the outlines of the poles being free from the deposit and retaining the original brightness of the iron. I have repeated this experiment a number of times in the presence of others, and it never fails to call forth the strongest expressions of pleasure, while I must confess that my own enthusiasm is aroused by it to an unusual extent. Fig. 3 shows at least the direction of the lines of deposit. It will here again be seen that they are at right angles to the lines of force, s was anticipated.

Although from the results already described the general direction of the lines of copper deposited can be predicted with a considerable degree of certainty for any given case, a final experiment was performed, with such an arrangement of the apparatus as to secure the strong magnetization of a point in the centre of the iron plate. The same magnet and battery were used as in the last experiment, but the magnet was so fixed in position that the line joining the two poles was perpendicular. Conical poles replaced those of truncated angular shape, and these were brought within about half an inch of each other. In this case the central point over the pole on which the vessel stood remained free from the deposit, while the ridges appeared in circles around this point, growing less and less strongly marked from the centre outward. These circles could be easily distinguished for a distance of nearly two inches from the pole—the largest circles thus having diameters of nearly four inches. Fig. 4 is intended to represent the appearance of the lines.

As a general result of these experiments it may be stated that *when copper is deposited from a solution of copper sulphate on a plate of iron in a magnetic field, it is arranged in ridges around the poles of the magnet, and in directions which are at right angles to the lines of force, and consequently, coincident with the lines marking the equipotential surfaces. Further, the outlines of the poles of the magnet are always sharply defined on the plate, as along these lines a portion of the iron of greater or less width is left unacted upon.*

It may be well here to give more specific directions in regard to the method of performing the experiments, in order to facilitate their repetition by others. The only difficulty is in the preparation of the iron plates. After many trials I have, for the present at least, found that plates can be most conveniently obtained in proper condition from ordinary ferrotype iron. Sheets of this may be obtained from any dealer in photographer's materials. The coating on the surface of the iron is removed by placing it in a bath of caustic soda for a short time, the process being hastened by heating. The plates, cut in sizes to suit the magnet to be used, are then bent up on all sides so as to form shallow vessels about a quarter to three-eighths of an inch in depth. To prevent rusting, it is better to leave the plates in the bath until they are needed. After a vessel is bent into proper shape it is washed

successively with water, a little ordinary concentrated hydrochloric acid, and again water. The bottom is dried, the vessel placed in position on the poles of the magnet, and the solution of copper sulphate poured in. The operations should be performed quickly, in order that the surface of the iron may be as bright as possible when the action begins. It should be observed, however, that the effects can be obtained distinctly without all these precautions, but for the best effects they are essential.

The plates appear best immediately after pouring off the solution. Then the copper has its proper color, and the parts of the iron which remain uncovered are bright; but very soon rusting begins, and before the plates are dry the color of the entire deposit, as well as of the unchanged iron, is that of the oxide of iron. All the original lines remain, however, fully as marked as at first. I have some plates which have remained for weeks unchanged, and which show the figures as clearly as on the day they were deposited. Of course, rubbing removes the deposit, so that, to be preserved, the plates should be protected in some way. I have tried photograph varnish, and this answers the purpose fairly well, though it causes the figures to appear less sharply defined than they do when uncovered.

Passing to a more important matter, we naturally ask, what is the cause of the phenomenon? In regard to this we can at present only speculate, and it is premature to speculate much on the subject as yet. There can be no doubt that the effects observed are to be ascribed to the action of magnetism, either on the iron plate or on the liquid, or on both. Experiment can decide between these possibilities. If the effect is due solely to magnetization of the iron, then non-magnetic metals will not exhibit similar phenomena; while, if it is due solely to the action of the magnet on the liquid, the same or similar effects should be obtainable with non-magnetic metals. The question thus left open will next occupy my attention. Whether, after all the facts are established which promise to be revealed in the course of the investigation thus begun, it will be possible to frame a satisfactory theory, remains to be seen. At all events, I propose to continue the study of the new set of phenomena.

In conclusion, it should be stated that a careful examination of the literature has failed to show that any experiments of the kind described in this paper have ever been performed. The only one I have found an account of which in any particular resembles mine is that of Jacobi.[1] This physicist desired to know whether iron

[1] Pogg. Annalen **149**, 341.

deposited by electrolysis in a magnetic field is itself magnetic. To determine this he arranged an apparatus thus: A candle covered with a thin, uniform layer of copper was placed in a cylinder containing a solution of an iron salt. The cylinder was then surrounded by a coil connected with a battery, and a current from another weak battery was passed through the iron solution, the copper cylinder forming the pole upon which the iron was deposited. After the action had continued for twenty-eight days the cylinder was removed, and it was found that the deposit was thicker at the ends than in the middle, but no *lines* of deposit were observed. It is questionable whether the action in this case is the same as that under consideration. I am inclined to think that the two are quite distinct phenomena, though it is possible that there is more resemblance than appears at first.

DETERMINATION OF CHROMIUM IN CHROME IRON ORE.

By H. N. Morse and W. C. Day.

When a determination of the chromium only is sought, the decomposition of chrome iron ore, according to our experience, can be best accomplished by fusing the material with potassium hydroxide in a wrought-iron crucible.

The method here described has, without exception, given us satisfactory results. From six to ten grams of potassium hydroxide are placed in a wrought-iron crucible (having the form of the ordinary porcelain crucible and a capacity of about 100 cc.) and gently heated until the evolution of steam ceases and the fused mass becomes tranquil. After cooling, the finely pulverized material, weighing not more than 0.5 gram, is placed upon the potassium hydroxide and evenly distributed over the surface. A flame just sufficient to thoroughly fuse the alkali is applied to the uncovered crucible, and the contents, as long as they remain in a fluid condition, frequently stirred with a piece of iron wire, which is allowed to remain in the crucible. The decomposition progresses rapidly, and the potassium hydroxide together with the soluble products of the decomposition soon begins to rise upon the sides of the crucible,

where it deposits itself in forms somewhat resembling the cauliflower. Within two or three hours the decomposition is complete, and the bottom of the crucible becomes dry. The crucible is then turned upon its side and the temperature of its under surface raised to a dull red heat. The incrustation on the interior of the crucible does not fuse at this temperature, but becomes rapidly yellow, owing to the oxidation of the chromium to chromate. At the end of two or three hours the oxidation is perfect. Portions of the incrustation retain a greenish color, however long the heating is continued ; but this is due to the presence of iron or manganese and not to unoxidized chromium.

After cooling, the crucible is placed in a porcelain evaporating dish and the contents removed by means of hot water. The solution, which at first has a greenish appearance owing to the presence of iron dissolved in the caustic potassa, is heated for some time in order to effect complete precipitation of the iron. The filtrate, which has a clear yellow color, is rendered slightly acid with pure dilute nitric acid, the aluminum precipitated with ammonia and washed by decantation. The chromate of potassium is then reduced and the silica rendered insoluble by evaporating to perfect dryness with an excess of hydrochloric acid. The residue is moistened with hydrochloric acid and treated with water.

It only remains to separate the chromium in the filtrate from magnesium and to determine it as chromic oxide. To do this we have preferred in each instance to first precipitate with barium carbonate.

We give here the data of twelve determinations upon material whose origin is unknown to us. Four of these (1–4) were made by ourselves, four (5–8) by Mr. A. G. Palmer, and the remainder (9–12) by Mr. W. S. Bayley, both students in this laboratory. The analyses reported were in each case made consecutively.

	Wt. of Ore taken.	Wt. of Cr_2O_3 found.	Percentage.
1.	0.3250	0.1343	41.32
2.	0.3465	0.1433	41.35
3.	0.3248	0.1343	41.36
4.	0.3383	0.1392	41.14
5.	0.2723	0.1120	41.12
6.	0.3955	0.1629	41.19
7.	0.3311	0.1358	41.02
8.	0.31285	0.1290	41.23
9.	0.3387	0.1392	41.10
10.	0.2995	0.1235	41.25
11.	0.3606	0.1478	41.00
12.	0.3007	0.1236	41.11

In order to assure ourselves that complete decomposition and oxidation had been effected, the same method of treatment was applied to the iron and aluminum precipitates as to the original material. This was done in the case of nine of the analyses here reported. But in no case was there any trace of chromium obtained from them. The average loss of the iron crucibles is about 0.2 gram. Much coarser material can be successfully analyzed by this than by the other methods in use. Its simplicity and economy also recommend it.

The only method on recórd, so far as we know, involving the use of potassium hydroxide for the decomposition of chrome iron ore, is that proposed by H. Schwarz,[1] who recommended fusion with potassium hydroxide in a silver crucible and addition of potassium chlorate to the fused mass. The decomposition by this method is doubtless easy and complete, but the rapidity with which the crucible is destroyed renders the method wholly impracticable.

JOHNS HOPKINS UNIVERSITY, *May* 1881.

Contributions from the Chemical Laboratory of Harvard College.

X.—ON FURFUROL AND CERTAIN OF ITS DERIVATIVES.

BY HENRY B. HILL.

[*Concluded from p.* 123.]

MUCOCHLORIC ACID.

Mucochloric acid was discovered in 1865 by Schmelz and Beilstein,[2] and since that time, as far as I know, it has never been further studied. The discoverers found its preparation so very laborious, and the yield which they obtained so small, that they made no extended investigation of it, but contented themselves with giving a short description of the acid, together with the analyses necessary to establish its composition. Although their account was certainly not encouraging, it seemed to me worth while to attempt its preparation, more especially in order to study the dichloracrylic

[1] Liebig's Annalen **69**, 212. [2] Ann. Chem. u. Pharm. Suppl. **3**, 280.

acid derived from it, and to compare this with the acid of the same composition which Wallach[1] had already made from chloralid. This investigation Mr. W. Z. Bennett undertook with me.

The method followed by Schmelz and Beilstein in making mucochloric acid was as follows: Pyromucic acid suspended in water was treated with chlorine at first in the cold and afterwards at boiling heat. When all action appeared to be over, the solution was somewhat concentrated on the water bath, and finally brought to crystallization by evaporation over sulphuric acid *in vacuo*. This method gave in our hands precisely the same discouraging quantitative results that Schmelz and Beilstein had obtained; and it was only after a long series of unsuccessful experiments that we succeeded in finding a simple modification of the method which enabled us to prepare material sufficient for investigation. We suspended the pyromucic acid in ten times its weight of water, cooled the whole well with ice, and passed in a rapid stream of chlorine until the liquid was thoroughly saturated. The temperature was carefully kept within a few degrees of the freezing point during this treatment with chlorine, and not unfrequently considerable quantities of the crystalline hydrate of chlorine separated. When the solution was saturated it was heated to boiling, after a few moments again cooled to 0°, and saturated once more with chlorine. When this operation had been repeated several times, crystals of mucochloric acid began to appear as the solution cooled. At first we filtered these crystals off, and subjected the filtrate to further treatment; but we found by experience that little or no product was gained after the sixth chlorination, and we, therefore, usually proceeded to this point before we removed the acid formed. We then collected the crystals which separated as the solution cooled, and evaporated the mother liquors on the water bath to the point of crystallization. The crystals were drained, pressed, and recrystallized from hot water. We further found it convenient to add to the pyromucic acid a small percentage of iodine. Although this was by no means essential, we found that our results were then more constant and the average yield greater. As the result of several preparations which we made in the course of the investigation, we obtained 129 grams of mucochloric acid from 202 grams of pyromucic acid. This corresponds to a little more than forty per cent. of the theoretical amount, as our average product, although

[1] Berichte der deutsch. chem. Gesellsch. **8**, 1580.

in single instances our yield has reached fifty per cent. The product made in this way crystallized from water in well-formed rhombic plates which in their properties agreed in every particular with the description of Schmelz and Beilstein. The acid melted at 125°, and was very soluble in alcohol or ether, sparingly soluble in cold water, readily in hot. Boiling benzol or chloroform dissolved it with readiness, while in carbonic disulphide or ligroin it was almost insoluble. The purity of our material was shown by the following analyses:

I. 0.7408 gram substance gave 0.7617 gram CO_2 and 0.0831 gram H_2O.

II. 0.5512 gram substance gave 0.5687 gram CO_2 and 0.0621 gram H_2O.

III. 0.2090 gram substance gave 0.3564 gram AgCl.

Calculated for $C_4H_2Cl_2O_3$.		Found.		
		I.	II.	III.
C	28.40	28.06	28.13	...
H	1.18	1.25	1.25	...
Cl	42.01	...	...	42.16

Although mucochloric acid appears to form derivatives in some respects more stable and readily studied than the corresponding derivatives of mucobromic acid, we have thus far taken up more in detail only the dichloracrylic acid, which may easily be made from it by the action of alkalies.

Dichloracrylic Acid.

In 1877 Wallach[1] obtained a dichloracrylic acid as a product of the reduction of chloralid. This acid was afterward more carefully studied by Wallach and Hunäus,[2] and quite recently Wallach[3] has published a paper still further describing the acid and its salts, and correcting the work of Hunäus in several important particulars. At the time this investigation was begun this acid was the only disubstituted acrylic acid known, and, since its constitution was fairly established by the mode of its preparation, it seemed desirable to prepare the dichloracrylic acid from mucochloric, in order to compare the two acids.

[1]Berichte der deutsch. chem. Gesellsch. **8**, 1580.
[2]Berichte der deutsch. chem. Gesellsch. **10**, 567. Ann. Chem. u. Pharm. **193**, 19.
[3]Ann. Chem. u. Pharm. **203**, 83.

The decomposition of mucochloric acid into dichloracrylic and formic acids, under the influence of alkalies, is much more neatly accomplished than the corresponding reaction with mucobromic acid. Under ordinary conditions, but little hydrochloric acid is split off, and the yield of dichloracrylic acid is nearly 90 per cent. of that required by the equation,—

$$C_4H_2Cl_2O_3 + H_2O = C_3H_2Cl_2O_2 + CH_2O_2.$$

We never have noticed in the preparation of dichloracrylic acid either chlorpropiolic acid or any compound corresponding to that which brompropiolic acid forms with dibromacrylic. We usually have dissolved mucochloric acid in quite an excess of potassic hydrate, allowed the solution to stand for a short time, acidified with hydrochloric acid, and extracted with ether. The dichloracrylic acid left on evaporation of the ether may be purified by melting it several times with a little water. When dried over sulphuric acid it gave the following results on analysis:

I. 0.5280 gram substance gave 0.4894 gram CO_2 and 0.0720 gram H_2O.

II. 0.3670 gram substance gave 0.3399 gram CO_2 and 0.0477 gram H_2O.

III. 0.1037 gram substance gave 0.2123 gram AgCl.

IV. 0.2674 gram substance gave 0.5420 gram AgCl.

	Calculated for $C_3H_2Cl_2O_2$.	Found.			
		I.	II.	III.	IV.
C	25.54	25.28	25.25	...	...
H	1.42	1.51	1.45	...	...
Cl	50.36	...	...	50.62	50.10

This dichloracrylic acid forms small rhombic prisms which volatilize rapidly on exposure to the air. It is readily soluble in water, alcohol, ether, or chloroform, and it also dissolves freely in boiling benzol, carbonic disulphide, or ligroin. It melts at 85–86°, and, when solidified by quick cooling, melts again at the same temperature. The β dichloracrylic acid of Wallach, on the other hand, melts at 76–77° and its melting point falls to 63–64° when melted and suddenly cooled.

Argentic Dichloracrylate, $AgC_3HCl_2O_2$. The silver salt was precipitated in the form of fine felted needles on the addition of

argentic nitrate even to a dilute solution of the acid. The salt was quite stable and could be recrystallized from hot water without any marked decomposition.

I. 0.5460 gram substance gave 0.2808 gram CO_2 and 0.0299 gram H_2O.

II. 0.4819 gram substance gave 0.2494 gram CO_2 and 0.0253 gram H_2O.

III. 0.2511 gram substance gave, by Carius' method, 0.2910 gram AgCl.

IV. 0.2078 gram substance gave, by Carius' method, 0.2401 gram AgCl.

V. 0.2089 gram substance, precipitated by HCl, gave 0.1209 gram AgCl.

VI. 0.6768 gram substance, precipitated by HCl, gave 0.3909 gram AgCl.

Calculated for $AgC_3HCl_2O_2$.		Found.					
		I.	II.	III.	IV.	V.	VI.
C	14.52	14.03	14.12	...	...	...	...
H	0.40	0.60	0.58	...	...	...	...
Cl	28.63	...	...	28.65	28.56	...	...
Ag	43.54	...	...	...	...	43.55	43.49

Baric Dichloracrylate, $Ba(C_3HCl_2O_2)_2.H_2O$. The barium salt was prepared by neutralizing the aqueous solution of the acid with baric carbonate and concentrating the solution upon the water bath. On cooling, the salt separated in rhombic plates which were permanent in the air, and did not lose in weight over sulphuric acid *in vacuo*.

I. 0.2185 gram of the salt lost, when heated to 80°, 0.0088 gram H_2O, and gave, on ignition with H_2SO_4, 0.1174 gram $BaSO_4$.

II. 0.1941 gram of the salt gave, on ignition with H_2SO_4, 0.1041 gram $BaSO_4$.

III. 0.2402 gram of the salt gave, on ignition with H_2SO_4, 0.1281 gram $BaSO_4$.

IV. 0.9167 gram of the salt lost, when heated to 80°, 0.0395 gram H_2O.

Calculated for $Ba(C_3HCl_2O_2)_2.H_2O$.		Found.			
		I.	II.	III.	IV.
Ba	31.49	31.59	31.53	31.36	...
H_2O	4.14	4.03	...	...	4.31

For the further characterization of this salt we determined its solubility in cold water by the method of V. Meyer.

I. 5.6625 grams of an aqueous solution, saturated at 18°, gave, on evaporation and ignition with H_2SO_4, 0.1956 gram $BaSO_4$.

II. 2.416 grams of a solution, saturated at 18.5°, gave 0.0801 gram $BaSO_4$.

These determinations give as the percentages of the anhydrous salt contained in the solutions saturated at 18° and 18.5° respectively:

I.	II.
6.28	6.19

Calcic Dichloracrylate, $Ca(C_3HCl_2O_2)_2.3H_2O$. The calcium salt, which was extremely soluble in water, was made by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long, flat radiating needles, which were permanent in the air, but slowly effloresced over sulphuric acid.

I. 0.4077 gram of the air-dried salt lost, on heating to 95–100°, 0.0580 gram H_2O, and gave, on ignition with H_2SO_4, 0.1488 gram $CaSO_4$.

II. 0.6163 gram of the air-dried salt lost, on heating, 0.0875 gram H_2O.

III. 0.3217 gram of the dried salt (II.), corresponding to 0.3749 gram of the air-dried salt, gave, on ignition with H_2SO_4, 0.1348 gram $CaSO_4$.

Calculated for $Ca(C_3HCl_2O_2)_2.3H_2O$.		Found.		
		I.	II.	III.
Ca	10.69	10.73	...	10.58
H_2O	14.43	14.23	14.20	...

Potassic Dichloracrylate, $KC_3HCl_2O_2$. The potassium salt crystallizes from a solution of mucochloric acid in an excess of potassic hydrate (1 : 4) when this is strongly cooled. Although it is quite soluble even in cold water, it may readily be purified by recrystallization from hot water. From concentrated solutions it crystallizes on cooling in long, slender needles, which are anhydrous.

I. 0.3054 gram of the salt gave, on ignition and evaporation with HCl, 0.1283 gram KCl.

II. 0.2159 gram of the salt gave 0.0908 gram KCl.

Calculated for $KC_3HCl_2O_2$.		Found. I.	II.
K	21.84	22.03	22.06

The foregoing results seemed to us to show with sufficient precision that our acid was essentially different from the β dichloracrylic acid of Wallach, since the two acids differed markedly in their physical properties, and their salts were also quite dissimilar. Following the analyses of Hunäus, Wallach[1] had assigned to the barium salt of the β dichloracrylic acid the formula $Ba(C_3HCl_2O_2)_2.5H_2O$, and to the calcium salt the probable formula $Ca(C_3HCl_2O_2).1\frac{1}{2}H_2O$; while the corresponding salts of our acid we had found to have the formulæ $Ba(C_3HCl_2O_2)_2.H_2O$ and $Ca(C_3HClO_2)_2.3H_2O$. Although the potassium salt of neither acid contained water of crystallization, one crystallized in plates, the other in needles.

Quite recently Wallach[2] has published the results of several determinations made since the publication of a preliminary notice[3] of our dichloracrylic acid. These determinations show that the formulæ which had previously been assigned to the barium and calcium salts of his acid were incorrect, and that they probably each contained two molecules of water. To these determinations, however, Wallach would attach but little weight for the identification of the acid, although he considers the isomerism of the two dichloracrylic acids to be fully established.

"Ich möchte aber nach den gemachten Erfahrungen diesen Bestimungen vorläufig keinen besonderen Werth für die *Charakterisirung* der Dichloracrylsäure aus Chloralid beilegen. Man wird besser thun, sich dafür an die scharf bestimmbaren Eigenschaften der *gemessenen freien* Säure und allenfalls an die tafelförmige Ausbildung des wasserfreien Kalisalzes, sowie an die angegebenen krystallographischen Daten des Baryumsalzes, anstatt an die bisher ausgeführten Wasserbestimmungen zu halten; für letztere müssen noch weitere Versuche vorbehalten bleiben. Jedenfalls muss aber der Zweck der obigen Angaben jetzt schon als erreicht bezeichnet werden: nämlich die völlige *Verschiedenheit der Dichloracrylsäure aus Chloralid* der nur die Formel $CCl_2{=}CH{-}CO_2H$ zukom-

[1] Ann. Chem. u. Pharm. **193**, 23. [2] Ibid. **203**, 83.
[3] Berichte der deutsch. chem. Gesellsch. **12**, 655.

men kann, *von der*, welche Bennett und Hill *aus Mucochlorsäure erhielten definitiv zu bestätigen*."[1]

Unfortunately we have as yet been unable to obtain either our acid or its barium salt in a form which would admit of crystallographic study. Still, the differences already established leave no reasonable doubt that the two acids are isomeric, and the acid from mucochloric acid may therefore be distinguished for convenience as the α dichloracrylic acid.

The behavior of this acid towards reagents has thus far been little examined. On boiling with an excess of baric hydrate, it is decomposed in essentially the same way as the dibromacrylic acid, baric malonate being formed in abundance. This decomposition with alkalies we have not followed further, since it was evident that chlorpropiolic acid should be the intermediate product formed ; and we wished not to interfere with the researches which Wallach had already undertaken with Bischof,[2] concerning the decomposition of β dichloracrylic acid by alkalies.

Although the acid does not take up bromine when heated with it to 100° in chloroform solution, it readily forms an addition product when heated for some time with undiluted bromine at 100°. The dichlordibrompropionic acid which is thus formed is at present under investigation in this laboratory.

Substituted Acrylic Acids from Brompropiolic Acid.

Mr. C. F. Mabery has studied with me some of the substituted acrylic acids which may readily be made by the addition of halogens or haloid acids to brompropiolic acid.

Dibromacrylic Acid of Fittig and Petri.

Brompropiolic acid dissolves easily in concentrated hydrobromic acid (b. pt. 126°), and, on standing for a short time, the solution deposits abundant crystals of a dibromacrylic acid, which is identical with that described by Fittig and Petri as resulting from the decomposition of tribromsuccinic acid. This acid may also be prepared to advantage from the solution of baric brompropiolate and baric bromide, which is obtained in the preparation of baric dibromacrylate by the action of baric hydrate upon mucobromic acid. It

[1] Loc. cit. 86.

[2] Berichte der deutsch. chem. Gesellsch. **11**, 751 ; **12**, 57.

is only necessary to precipitate the barium with dilute sulphuric acid, and to concentrate the solution upon the water bath. The acid which separates as the solution cools is easily purified by recrystallization.

From a hot concentrated solution the acid falls at first as an oil, but, after the solution has cooled somewhat, it separates in pearly scales, which melt at 85–86°. In analysis they gave the required percentage of bromine.

0.2614 gram of substance gave 0.4283 gram AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.
Br	69.57	69.72

The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the solution made according to V. Meyer's method, and evaporating the filtered solution with sulphuric acid.

I. 12.5364 grams of a solution, saturated at 20°, gave 0.2070 gram $BaSO_4$.

II. 11.6241 grams of a solution, saturated at 20°, gave 0.1712 gram $BaSO_4$.

III. 8.4358 grams of a solution, saturated at 20°, gave 0.1248 gram $BaSO_4$.

IV. 10.6740 grams of a solution, saturated at 20°, gave 0.1581 gram $BaSO_4$.

As the result of these determinations, we find that an aqueous solution of the acid, saturated at 20°, contains the following percentages:

I.	II.	III.	IV.
3.16	2.91	2.92	2.93

Fittig and Petri found that the dibromacrylic acid made from tribromsuccinic gave at 20° a solution which contained 3.355 per cent. of the acid.

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.2H_2O$. An aqueous solution of the acid was neutralized with baric carbonate, and the filtered solution evaporated on the water bath. On cooling the barium salt crystallized in rectangular plates, whose angles were, however, often more or less modified.

The air-dried salt lost, on heating to 100°, two molecules of water.

I. 1.4018 gram of air-dried salt lost at 100° 0.0226 gram H_2O.

II. 0.4644 gram of air-dried salt lost at 100° 0.0261 gram H_2O.

III. 0.5086 gram of air-dried salt lost at 100° 0.0299 gram H_2O.

Calculated for $Ba(C_3HBr_2O_2)_2.2H_2O$.		Found. I.	II.	III.
H_2O	5.71	5.62	5.62	5.88

The anhydrous salt then gave:

I. 0.3425 gram of substance, dried at 100°, gave, on ignition, 0.1353 gram $BaSO_4$.

II. 0.4383 gram of the salt, dried at 100°, gave 0.1723 gram $BaSO_4$.

III. 0.2934 gram of the salt, dried at 100°, gave 0.1153 gram $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2$.		Found. I.	II.	III.
Ba	23.03	23.23	23.11	23.10

Fittig and Petri found in two determinations of water in the barium salt of their acid a somewhat higher percentage (6.73 and 7.27), and therefore assign it the formula $Ba(C_3HBr_2O_2)_2.2\frac{1}{2}H_2O$—(calculated 7.03 per cent.)

The solubility of the salt we determined by V. Meyer's method.

I. 3.9749 grams of a solution, saturated at 23°, gave, on evaporation with H_2SO_4 and ignition, 0.1748 gram $BaSO_4$.

II. 3.9148 grams of a solution, saturated at 20°, gave 0.1719 gram $BaSO_4$.

According to these determinations, the aqueous solution, saturated at 20°, contained the following percentages of the anhydrous salt:

I.	II.
11.23	11.21

Calcic Dibromacrylate $Ca(C_3HBr_2O_2)_2.3\frac{1}{2}H_2O$. The calcium salt we prepared by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long, radiating needles.

I. 0.5625 gram of the air-dried salt lost, when heated to 10°, 0.0668 gram H_2O, and gave, when ignited with H_2SO_4, 0.1356 gram $CaSO_4$.

II. 0.3460 gram of the salt lost at 100° 0.0394 gram H_2O and gave 0.0850 gram $CaSO_4$.

Calculated for $Ca(C_3HBr_2O_2)_2.3\frac{1}{2}H_2O$.		Found. I.	II.
Ca	7.13	7.09	7.22
H_2O	11.23	11.88	11.39

Fittig and Petri found in two determinations of water, in the calcium salt of their acid, the percentages 11.56 and 11.47, from which they calculate the formula with $3\frac{1}{2}$ molecules of water, given above.

The physical properties of the acid and the analyses of the barium and calcium salts leave no doubt of the identity of this dibromacrylic acid with that described by Fittig and Petri, although our results differ slightly in some respects from theirs. The acid from tribromsuccinic acid we have made only in sufficient quantity to assure ourselves that no qualitative differences are to be detected in the properties of the two acids, or in the habit of several of their salts.

Iodbromacrylic Acid.

Brompropiolic acid dissolves readily in concentrated hydriodic acid (b. pt. 127°), and so rapid is the action that in a few moments the solution is filled with crystals of the addition product. The crude acid is pressed between folds of filter paper and recrystallized from hot water.

The acid separates from a hot, concentrated solution as an oil, but at a lower temperature it crystallizes in pearly scales, which melt at 110°. The acid is readily soluble in alcohol, ether or chloroform, but sparingly in benzol, carbonic disulphide, or ligroin.

I. 0.3800 gram substance gave 0.1828 gram CO_2 and 0.0307 gram H_2O.

II. 0.2945 gram substance gave 0.4480 gram AgBr+AgI.

Calculated for $C_3H_2BrIO_2$.		Found. I.	II.
C	12.99	13.12	...
H	0.70	0.90	...
Br, I	74.73	...	74.47

The solubility of the acid in cold water we determined by neutralizing the saturated aqueous solution, made according to the method of V. Meyer, with baric carbonate, and evaporating with sulphuric acid.

I. 11.1382 grams of a solution, saturated at 20°, gave 0.0785 gram $BaSO_4$.

II. 10.8923 grams of a solution, saturated at 20°, gave 0.0783 gram $BaSO_4$.

According to these determinations, the aqueous solution of the acid, saturated at 20°, contained the following percentages:

I.	II.
1.68	1.71.

For the further characterization of the acid, we prepared the barium, calcium and silver salts.

Baric Iodbromacrylate, $Ba(C_3HBrIO_2)_2.3H_2O$. The barium salt we made by saturating the aqueous solution of the acid with baric carbonate and concentrating on the water bath. From concentrated solutions it crystallizes in fine needles; from more dilute in rectangular plates. The air-dried salt contains three molecules of water, which it loses *in vacuo* over sulphuric acid.

I. 0.4660 gram of air-dried salt lost *in vacuo* over H_2SO_4 0.0360 gram H_2O, and lost then nothing at 80°.

II. 0.2832 gram of air-dried salt lost *in vacuo* over H_2SO_4 0.0208 gram H_2O, and afterwards, when heated to 80°, 0.0011 gram.

	Calculated for $Ba(C_3HBrIO_2)_2.3H_2O$.	Found. I.	II.
H_2O	7.27	7.73	7.35

0.4427 gram of the dried salt gave, on ignition with H_2SO_4, 0.1498 gram $BaSO_4$.

	Calculated for $Ba(C_3HBrIO_2)_2$.	Found.
Ba	19.88	19.90

The solubility of the salt in cold water we also determined.

I. 2.0636 grams of a solution saturated at 20° gave, on evaporation with H_2SO_4, 0.0967 gram $BaSO_4$.

II. 3.0991 grams of a solution saturated at 20° gave 0.1457 gram $BaSO_4$.

From these determinations it follows that the aqueous solution, saturated at 20°, contains the following percentages of the anhydrous salt:

I.	II.
13.86	13.90

Calcic Iodbromacrylate, $Ca(C_3HBrIO_2)_2.3\frac{1}{2}H_2O$. The calcium salt resembles the barium salt closely in appearance, but is more soluble in water. The air-dried salt loses its crystal water completely *in vacuo* over sulphuric acid, or when heated to 80°.

I. 0.7622 gram of the air-dried salt lost 0.0771 gram H_2O at 80°.

II. 0.7172 gram of the air-dried salt lost 0.0698 gram H_2O at 80°.

	Calculated for $Ca(C_3HBrIO_2)_2.3\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	9.89	10.12	9.73

0.6518 gram of the salt dried *in vacuo* gave, on ignition with H_2SO_4, 0.1465 gram $CaSO_4$.

	Calculated for $Ca(C_3HBrIO_2)_2$.	Found.
Ca	6.76	6.61

Argentic Iodbromacrylate, AgC_3HBrIO_2. The silver salt was precipitated from an aqueous solution of the acid by the addition of argentic nitrate. It formed short, clustered needles, which could be recrystallized from water, with but little decomposition.

I. 0.4509 gram of substance gave 0.1597 gram AgCl and 0.0063 gram metallic silver.

II. 0.7458 gram substance gave, on precipitation with HBr, 0.3635 gram AgBr.

	Calculated for AgC_3HBrIO_3.	Found. I.	Found. II.
Ag	28.13	28.05	27.99

With hydrochloric acid, the addition takes place much more slowly; still, after long standing, the chlorbromacrylic acid is formed.

Of the products formed by the addition of halogens to brompropiolic acid, we have thus far examined in detail only the tribromacrylic, although we have also made the diiodbromacrylic by the addition of iodine.

Tribromacrylic Acid.

Tribromacrylic acid may easily be made by adding slowly a slight excess of bromine to an aqueous solution of brompropiolic acid. The color of the bromine gradually disappears, and the product of the reaction separates partially in the form of an oil. This oil gradually solidifies, and more of the same product can be extracted with ether from the aqueous solution. The resulting solid must be well pressed out, and may then be recrystallized from chloroform, or, better, from benzol. Thus prepared, it forms colorless, oblique prisms, which are very soluble in ether or alcohol, less soluble in cold chloroform or benzol, readily in hot, and soluble in carbonic disulphide or ligroin. It is but sparingly soluble even in boiling water. Melting point, 118°.

I. 0.3449 gram of the acid gave 0.1428 gram CO_2 and 0.0183 gram H_2O.

II. 0.1782 gram substance gave 0.3229 gram AgBr.

III. 0.1433 gram substance gave 0.2625 gram AgBr.

	Calculated for $C_3HBr_3O_3$.	Found.		
		I.	II.	III.
C	11.65	11.29	...	...
H	0.32	0.59		
Br	77.67	...	77.13	77.94

The acid when boiled with an excess of baric hydrate is hardly affected, although it is slowly decomposed by a boiling alcoholic solution of potassic hydrate. We have as yet isolated no products of this decomposition.

The solubility of the acid in water at ordinary temperatures we have also determined by the method of V. Meyer.

I. 11.4429 grams of a solution, saturated at 20°, gave, after neutralization with $BaCO_3$ and evaporation with H_2SO_4, 0.0597 gram $BaSO_4$.

II. 12.7846 grams of a solution, saturated at 20°, gave 0.0643 gram $BaSO_4$.

According to these determinations, the aqueous solution of the acid saturated at 20° contains the following percentages:

I.	II.
1.38	1.33

Baric Tribromacrylate, $BaC_3Br_3O_2.3H_2O$. The barium salt we made by neutralizing the acid with a solution of baric hydrate. On cooling the concentrated solution, it crystallizes in long needles, which effloresce over sulphuric acid.

I. 0.7888 gram of the air-dried salt lost over H_2SO_4 0.0532 gram H_2O.

II. 0.7585 gram of the air-dried salt lost *in vacuo* over H_2SO_4 0.0506 gram H_2O.

III. 0.4900 gram of the air-dried salt lost at 80° 0.0324 gram H_2O.

IV. 0.7024 gram of the anhydrous salt gave, on ignition with H_2SO_4, 0.2185 gram $BaSO_4$.

V. 0.4486 gram of the anhydrous salt gave 0.1398 gram $BaSO_4$.

	Calculated for $Ba(C_3Br_3O_2)_2.3H_2O$.	Found. I.	Found. II.	Found. III.
H_2O	6.68	6.75	6.67	6.61

	Calculated for $Ba(C_3Br_3O_2)_2$.	Found. IV.	Found. V.
Ba	18.20	18.29	18.32

The solubility of this salt in cold water was determined by the method of V. Meyer.

I. 3.2130 grams of a solution saturated at 20° left, on evaporation with H_2SO_4 and ignition, 0.2349 gram $BaSO_4$.

II. 2.9600 grams of a solution saturated at 20° gave 0.2170 gram $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
23.62	23.69

Calcic Tribromacrylate $Ca(C_3Br_3O_2)_2.H_2O$. The calcium salt was made by warming the acid with water and calcic carbonate. It crystallized in needles which were permanent in the air, but lost in weight over sulphuric acid.

I. 0.4924 gram of the air-dried salt lost at 80° 0.0099 gram H_2O.

II. 0.8678 gram of the air-dried salt lost at 80° 0.0248 gram H_2O.

III. 0.4794 gram of the anhydrous salt gave, on ignition with H_2SO_4, 0.1001 gram $CaSO_4$.

IV. 0.8266 gram of the anhydrous salt gave, on ignition with H_2SO_4, 0.1707 gram $CaSO_4$.

	Calculated for $Ca(C_3Br_3O_2)_2.H_2O$.	Found. I.	II.
H_2O	2.67	2.01	2.86

	Calculated for $Ca(C_3Br_3O_2)_2$.	Found. III.	IV.
Ca	6.10	6.14	6.07

Argentic Tribromacrylate, $AgC_3Br_3O_2$. The silver salt is precipitated when argentic nitrate is added to an aqueous solution of the acid, but is more readily prepared from a solution of the acid in diluted alcohol. The salt is tolerably stable, and crystallizes in small, six-sided plates.

0.5267 gram of the salt gave 0.1848 gram AgCl.

	Calculated for $AgC_3Br_3O_2$.	Found.
Ag	25.96	26.40

Mr. Mabery has undertaken the study of the chlorbromacrylic and diiodbromacrylic acid, and will present the results of these investigations in a separate paper.

Theoretical Considerations.

Schmelz and Beilstein,[1] from a comparison of the formula of mellitic acid, $C_4H_2O_4$ (as it was then written), with that of mucobromic acid, $C_4H_2Br_2O_3$, were led to suspect a close connection between the two; but their investigations undertaken with the hope of proving this point yielded negative results.

In 1869, Limpricht[2] suggested that a series of compounds, among which were furfurol and its derivatives, contained a ring of four carbon atoms, and that they were therefore derived from an hypothetical hydrocarbon,—

$$\begin{array}{c} H-C=C-H \\ \;\;\;\,|\;\;\;\;\;| \\ H-C=C-H \end{array}$$

just as the various compounds of the aromatic series were derived from benzol. As the formula which naturally suggested itself for mucobromic acid he gives,—

$$\begin{array}{c} HOC=COHO \\ |\;\;\;\;\;\;| \\ BrC=CBr. \end{array}$$

[1] Ann. chem. u. Pharm. Suppl. 3, 280. [2] Berichte der deutsch. chem. Gesellsch. 2, 212.

although I am at a loss to know precisely how this formula is to be interpreted. This hypothesis received temporary support from the discovery of the so-called tetraphenol by Limpricht and Rohde;[1] but further experiments made in Limpricht's laboratory failed to sustain it, and in the subsequent detailed account of these investigations[2] no allusion is made to it. In this paper Limpricht described the formation of fumaric acid by the action of bromine and water upon pyromucic acid, as well as the substance $C_4H_4O_3$, which he called fumaric acid aldehyde, and regarded as the product from which mucobromic acid was derived by substitution. In 1877 Baeyer[3] showed that this latter substance was in fact the half-aldehyde of fumaric acid, in that it could be converted into fumaric acid by the action of argentic oxide. At the same time he pointed out the difficulty of supposing that mucobromic acid, which empirically was a substitution-product from this aldehyde, could be formed from it by the direct action of bromine.

In 1878 Wallach and Bischoff[4] published a paper upon the action of alkalies upon the β dichloracrylic acid, which Wallach[5] had previously made by the reduction of chloralid. In a subsequent paper[6] upon the same subject they assumed that the structure of the dibromacrylic acid from mucobromic, which O. R. Jackson and I[7] had shortly before described in a preliminary notice, was established quite surely by its ready conversion into malonic acid, and Wallach was therefore led to append a note containing a suggestion which he had previously made, that the constitution of mucobromic acid was probably represented by the formula—

$$CBr_2{=}CH{-}CO{-}COOH.$$

In 1879 Toennies,[8] in investigating the action of bromine upon dibrompyromucic acid[9] in Baeyer's laboratory, found that a substance, $C_4H_2Br_2O_2$, was formed according to the equation—

$$C_5H_2Br_2O_3 + Br_2 + H_2O = C_4H_2Br_2O_2 + CO_2 + 2HBr,$$

and that this could readily be converted into mucobromic by oxidation. This mode of formation led Toennies to the conclusion that mucobromic acid was the half-aldehyde of dibromfumaric acid.

[1]Berichte der deutsch. chem. Gesellsch. **3**, 90. [2]Ann. Chem. u. Pharm. **165**, 278.
[3]Berichte der deutsch. chem. Gesellsch. **10**, 1362. [4]Ibid. **11**, 751. [5]Ibid. **8**, 1580.
[6]Ibid. **12**, 57. [7]Ibid. **11** 1671. [8]Ibid. **12**, 1202. [9]Ibid. **11**, 1088.

Further investigation in this direction Toennies relinquished, in order to avoid interference with my work.

At the time of the publication of this paper by Toennies my own experiments had shown that this view was in part correct. The conversion of mucobromic acid by the action of argentic oxide or other oxidizing agents into the dibrommaleic acid of Kekulé showed with sufficient precision that it was the half-aldehyde of this acid. On the other hand, it was evident that the dibrommaleic acid itself did not belong to the fumaric series, as could fairly be inferred from its mode of preparation; but that it was in reality a substituted maleic acid, since it could be carried unchanged through its anhydride.

A more direct proof of this fact was furnished by the discovery by Bandrowski[1] of an isomeric acid of higher melting point, which could be converted into this by distillation.

Although it cannot be said that the constitution of fumaric and maleic acids is definitely established, the brilliant researches recently published from Fittig's laboratory leave but little doubt that the formula of maleic acid is—

$$\begin{array}{l} \quad CH_2—COOH \\ \quad\ \ | \\ =C—COOH. \end{array}$$

If this view of its structure be adopted, the structure of mucobromic acid must be represented by one of the formulæ—

$$\begin{array}{l} \quad CBr_2—CHO \\ \quad\ \ | \\ =C—COOH \end{array} \qquad \begin{array}{l} \quad CBr_2—COOH \\ \quad\ \ | \\ =C—CHO \end{array}$$

The ease with which it is decomposed, even in the cold, by alkalies and the aldehyde group thus converted into formic acid, would possibly incline one to adopt the first of these formulæ.

Unfortunately, no independent evidence concerning the position of the bromine atoms can as yet be drawn from the constitution of the dibromacrylic acid, which is formed at the same time, since

[1] Ibid. 12, 1232.

none of its reactions give a clew to its structure. It may only be asserted, with tolerable certainty, that its formula is not—

$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

since the corresponding chlorinated acid made from mucochloric acid appears to be essentially different from the dichloracrylic acid of Wallach, and the formation of the latter from chloralid shows its formula to be—

$$\begin{array}{l} CCl_2 \\ \| \\ CH \\ | \\ COOH. \end{array}$$

If the structure of mucobromic acid is represented by one of the formulæ given above, it follows that the dibromacrylic acid obtained from it has one of the forms—

$$\begin{array}{l} \quad CBr_2H \\ \quad\ | \\ =C \\ \quad\ | \\ \quad COOH \end{array} \qquad\qquad \begin{array}{l} =CH \\ \quad | \\ \quad CBr_2 \\ \quad | \\ COOH. \end{array}$$

The formation of a tribrompropionic acid, melting at 116–117° by the addition of hydrobromic acid, would in itself be a sufficient reason for rejecting the second formula, if the structure of the tribrompropionic acid, melting at 92°, could be shown to be—

$$\begin{array}{l} CH_2Br \\ | \\ CBr_2 \\ | \\ COOH. \end{array}$$

Although this is the constitution assigned to it by Michael and Norton,[1] it is evident that this formula is based upon a pure assumption concerning the structure of the α monobromacrylic acid from which it is made.

[1]This Journal, 2, 18.

No more decisive arguments against the second formula can be drawn from the reactions or the derivatives of the dibromacrylic acid, although the formation of malonic acid follows more simply from the first formula, and the forms—

$$\begin{array}{l} C= \\ \| \\ CH \\ \;\; Br \end{array} \qquad \text{and} \qquad \begin{array}{l} C= \\ \| \\ CBr \\ \;| \\ COOH \end{array}$$

which the second formula renders necessary for bromacetylen and brompropiolic acids, seem hardly in its favor. It would therefore seem probable that the structure of mucobromic acid is—

$$\begin{array}{l} \;\;\; CBr_2\text{—}CHO \\ \;\;\;\;\;| \\ =C\text{—}COOH. \end{array}$$

The close connection between the disubstituted acrylic acids derived from mucobromic and mucochloric acids and maleic acid makes their further study extremely desirable, more especially in order to obtain additional evidence bearing upon the position of the halogen atoms. Investigations in this direction are now in progress in this laboratory.

IV.—DINITROPARADIBROMBENZOLS AND THEIR DERIVATIVES.[1]

By W. D. Schoonmaker and J. A. Van Mater.

In the second paper of this series a compound was described which was obtained by the nitrition of β-dinitroparabromanilidobenzol. This compound, β-dinitroparabromdinitroanilidobenzol, owing to the entrance of the two nitro-groups, became reactive toward alkalies, and, on treatment with sodic hydrate, the formation of a salt appeared to take place. The production of this compound in large quantities would, it was hoped, afford us an oppor-

[1] The former papers of this series, by P. T. Austen, were published in the Amer. Jour. Sci. and Arts, Aug. 1876, Feb. 1877, July 1878.

tunity of studying various interesting derivatives; for the easy substitution of the bromine atom would allow of the substitution of a large number of basic rests. As the preparation of the compound by treatment of the β-dinitroparadibrombenzol with aniline was very roundabout, owing to the difficulty of separating the β-compound from the other isomers, we concluded to try the effect of heating the β-dinitroparabromphenol with aniline, in the hope that the large number of negative groups present would render the hydroxyl capable of substitution by a positive residue. It also appeared probable that if this reaction did not take place, the bromine atom might be open to substitution.

A number of experiments were made in which the phenol was heated with aniline in a closed tube from one to five hours at 100° and 160°. The result, however, was negative. A reaction had taken place, but the nitro-groups seemed to have acted on the aniline, producing an uninviting tar. No evolution of ammonia was observed, so that the reaction is different from that of picric acid on aniline, whereby ammonia is copiously evolved.

In the hope of obtaining an amido derivative of the phenol, it was reduced with tin and hydrochloric acid. The reduction took place easily. On evaporating the colorless solution freed from tin by precipitation with hydrogen sulphide, it became rapidly colored, and a black pulverulent substance separated.

We were not able with the means at our control to so conduct the operation as to avoid the oxidation. The black substance was insoluble in alcohol, but dissolved in concentrated sulphuric acid with a superb blue color, and did not fuse at 250°. It is probably an azoxycompound. A careful examination of it will be carried out as soon as a sufficient quantity can be obtained.

β-*Dinitroparabromphenetol*, $C_6H_2(NO_2)_2BrOC_2H_5$.

Some pure phenol silver salt, made by boiling the phenol in alcoholic solution with silver nitrate and a slight excess of silver oxide, was boiled in a flask with a return condenser with ethyl iodide. The reaction took place easily, as was shown by the change from the brilliant red of the silver salt to the yellow of the silver iodide. The whole was evaporated to dryness on a water bath, and extracted with boiling dilute alcohol.

The substance purified by repeated crystallizations from alcohol, formed small, light needles of a pearly color, fusing at 66° (uncorr.),

very easily soluble in alcohol and hot water. It is decomposed in the cold by sodic hydrate solution with regeneration of phenol. An analysis gave:

	Calculated for $C_6H_2(NO_2)_2BrOC_2H_5$.	Found. I.	II.
Br	27.50	27.82	27.79

Atomic Migration in the Mononitroparadibrombenzol Molecule.

In nitrating paradibrombenzol with a mixture of sulphuric acid and the strongest fuming nitric acid, it was remarked by Dr. Austen that small amounts of other dinitro-compounds than the α, β and γ appeared. The most marked among these was a dinitro-compound with a fusing point of 120°.

The yield of the three isomers already described seemed also to vary with the time, degree of heat and strength of the acids. As but little is known in regard to the causes which determine the formation of several isomers at the same time, we concluded to experiment with nitrition mixtures of various strengths. Fifty grams of paradibrombenzol were nitrated by boiling for three hours with a mixture of 160 grams of fuming nitric acid of 1.41 sp. gr. and an equal volume of concentrated sulphuric acid. After nitrition the whole was poured into cold water, and the separated nitro-compound allowed to harden. The resulting cake was dissolved in dilute alcohol, and boiled with potassium nitrite to convert[1] the β-dinitroparadibrombenzol into potassium β-dinitroparabromphenylate. The whole was then evaporated nearly to dryness, to drive off the alcohol, after which the mass was thoroughly extracted with boiling water. In this manner the β-dinitroparadibrombenzol was entirely removed as potassium β-dinitroparabromphenylate, which is easily soluble in boiling water, while the other nitro-compounds were left as a cake at the bottom. The amount of β-dinitro-isomer formed was small. The cake was dissolved in carbon disulphide and allowed to crystallize. On standing, a heavy crop of crystals was obtained. These were purified by repeated crystallizations from alcohol. The substance thus obtained proved to be the known mononitroparadibrombenzol, fusing at 84°, and giving, on analysis,

	Calculated for $C_6H_3(NO_2)Br_2$.	Found.
Br	56.94	56.77

[1] See Am. J. Sci. **16**, 5.

We were unable to obtain even a trace of the α-dinitro-isomer. From this it would appear that with acids of a certain strength, only the β-dinitroparadibrombenzol is formed. Whether the α and γ isomers are subsequently produced from the β by atomic migration, or by direct nitrition from the original dibrombenzol, we cannot say. It would appear probable from the above, however, that in the nitrition with the strong acid, in which case the three isomers are produced, the three are not formed simultaneously, but that the β-compound is produced first. The mother-liquor of the crystallizations from carbon disulphide on evaporation yielded decreasing amounts of the above substance. The liquor was evaporated to dryness and kept for some time on a water-bath to expel all traces of the carbon disulphide. In this manner a yellow oil was obtained resembling the substance which has been considered as the γ-dinitroparadibrombenzol. Instead of reacting easily with alcoholic ammonia, however, it remained unacted upon after standing with it for a week. An analysis showed this oil to be a liquid mononitrodibrombenzol.

	Calculated for $C_6H_3(NO_2)Br_2$.	Found.
Br	56.94	57.41

Several repetitions of the above experiments, substantially the same but varying in details of manipulation, gave the same results, viz. a small yield of β-dinitroparadibrombenzol, a large yield of mononitroparadibrombenzol, a considerable yield of the liquid mononitrodibrombenzol.

According to our present theory there can be but one mononitroparadibrombenzol, hence the liquid mononitrodibrombenzol which is produced must be formed by atomic migration. It was not clear, however, whether the mononitroparadibrombenzol was first formed and the liquid isomer from it by atomic migration, or whether a migration took place in the paradibrombenzol forming an isomeric dibrombenzol which then was nitrated.

To determine this, some pure mononitroparadibrombenzol was boiled with the nitrition mixture above described. The resulting product was extracted with potassium nitrite in the usual manner. Small amounts of the β-dinitro-compound had been formed. The residues were nitrated again, and extracted with potassium nitrite. This process was repeated three times. At each nitrition the mass left after extraction with the nitrite became softer, showing an

increase in the amount of oil. The unchanged monitroparadibrombenzol was then removed from the cake by crystallization from alcohol. The alcoholic mother-liquor gave on evaporation an oil which, on analysis, proved to be the isomeric mononitrodibrombenzol.

Calculated for $C_6H_3(NO_2)Br_2$.		Found.[1] I.	II.
Br	56.94	57.65	57.29

This shows, then, that the atomic migration takes place *after* the introduction of the nitro-group.

We hope to be able to reduce the liquid mononitrodibrombenzol, and by splitting off the amido group from the resulting dibromaniline, to obtain the dibrombenzol of which it is a derivative. So far the reduction has not been successful. Tin and hydrochloric acid give a tar from which we have not been able to obtain any defined compound.

The liquid mononitrodibrombenzol is not affected by alcoholic ammonia under pressure at 100°. Some reaction takes place, however, at 160°.

To ascertain if the atomic migration was simply the effect of heat independent of the acid, some pure mononitroparadibrombenzol was heated at 250°–300° in capillary tubes dipping in sulphuric acid. The substance evaporated so rapidly that no observation could be made. Portions were then heated in small closed tubes in an air bath, but they exploded with great violence. To avoid this, combustion tube was used. About a gram was heated in a closed combustion tube about four inches long. As yet we have observed no indications of the formation of the oily isomer.

The above investigation was conducted under the direction of Prof. P. T. Austen.

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[1]Analyses of different nitritions.

ON THE MOLECULAR WEIGHT OF HYDROFLUORIC ACID.[1]

By Prof. J. W. Mallet, F. R. S.

The analogies of fluorine with the halogens on the one hand and with oxygen on the other have often been remarked upon. The general resemblance of fluorine compounds to the corresponding compounds of chlorine is manifest, and the two elements are usually classed together; but some striking differences force themselves upon the attention, such as those existing between the chloride and fluoride of calcium, chloride and fluoride of silver, etc., and the marked tendency of the fluorides to the formation of double salts with formulæ analogous to those of oxygen compounds, as well as the formation of many salts including both oxygen and fluorine, suggests some close natural relation between these elements themselves.

When the principle of quantivalence or atomicity first began to assume distinct shape, it became a matter of special interest to decide whether fluorine should be classed with chlorine amongst the monad elements, with the formula HF for hydrofluoric acid, and the atomic weight 19 for fluorine itself, or should be placed with oxygen amongst the dyads, writing H_2F for hydrofluoric acid, and assuming the atomic weight of fluorine as 38. For some time, although analogies were chiefly in favor of the former view, no direct evidence was available for the settlement of this question, but in 1869 it seemed to be supplied by the researches of Gore,[2] who, heating silver fluoride in contact with an equivalent quantity of pure and dry hydrogen, observed that "one volume of hydrogen in uniting with fluorine produces, not simply one volume of gaseous product, as it does when uniting with oxygen, but two volumes, as in the case of its union with chlorine." Further on, in the same paper, after giving his results as to the amount of silver in the fluoride used, he says: "These results, combined with the foregoing experiments on molecular volume, agree with the conclusion that a volume of hydrogen weighing 1 unites with 19 parts by weight of fluorine to form 2 volumes of hydrofluoric acid, and that

[1]The substance of this paper was verbally presented, by invitation, at the meeting of the National Academy of Sciences at Washington, April 22, 1881.

[2]Philosophical Transactions for 1869. A further paper, on silver fluoride, appeared in 1870.

the specific gravity of gaseous anhydrous hydrofluoric acid is ten times the amount of that of hydrogen."

Gore's experiments were made with somewhat small quantities of the materials used (about a gram of silver fluoride and 90 or 100 cubic centimetres of hydrogen), and in opaque vessels of platinum, the volume assumed by the gaseous hydrofluoric acid being ingeniously determined by raising or lowering the cylindrical platinum receiver, so that the level of the mercury in which it was placed remained the same inside and out, and reading off an external scale. The whole apparatus was heated in an air-bath to 93°–100°C. before making the final reading. It is stated that fourteen separate attempts were made to ascertain the volume of gaseous product formed, but the numerical results of only two of these are given. They seem fairly to establish the fact that at temperatures near 100° hydrofluoric acid exists as HF, 93.3 and 98.5 per cent. respectively of the theoretical volume being obtained after allowance for expansion at the temperature employed. The atomic weight of fluorine is thus established as 19, not 38.

Certain measurements of the gaseous acid are, however, given for lower temperatures, though far above the boiling point (67° F., as found by Gore himself=19.5° C.) which represent distinctly smaller volumes. Thus at 139° F. (59.5° C.) the volume was but 85.8 per cent. of that required by theory, and at 160° F. (71° C.) it was 88.1 per cent.

Hence it seemed still desirable to try to ascertain whether the acid exhibits a different but definite vapor density at a temperature nearer the boiling point, though high enough to preclude any actual liquid acid remaining, operating on quantities large enough to give decisive results with even rough weighings, and if possible in transparent or translucent vessels. With this object in view I have made the following experiments.

Perfectly pure Greenland cryolite, carefully selected in choice fragments, was pulverized in a clean iron mortar, heated to 300° C. for some time, and transferred while still warm to a well dried and warm bottle. Sulphuric acid was prepared of full strength by adding to a quantity of the purified acid of 95 or 96 per cent. a small excess of pure sulphur trioxide, and passing for several hours a well dried and gently warmed current of air through the liquid ; this was also preserved in a well stoppered bottle until needed. The cryolite and acid were heated together in a leaden retort, the capital of

which was clamped on without lute, and the hydrofluoric acid vapor given off was conducted downwards through a worm of leaden tube, 6 mm. in interior diameter and 3.5 metres long, surrounded by crushed ice, into a leaden bottle cooled by a freezing mixture of ice and salt. The interior of all the leaden apparatus had been previously crusted over by passing hydrofluoric acid vapor through for some time. The joints were made by simply wrapping tightly with lead foil, and ligating with wire. The quantity of the materials used was such as to produce eight times the amount of hydrofluoric acid necessary to fill with vapor the leaden bottle and the flask and connecting tubes to be afterwards used, even assuming the highest vapor density that could well be expected.

The flask in which the vapor was to be weighed was of good Bohemian glass, and held nearly 4½ litres, being as large as could be well managed in the balance case. It was slung in a light network of platinum wire, with a suspending ring at top, and was, after thorough drying, carefully coated over the whole inside surface with clear, colorless paraffine,[1] poured in in the melted state, and evenly distributed by turning round and round the gently-warmed flask. The melting point of the paraffine was 56° C., well above the temperature to be afterwards applied. The neck of the flask was accurately fitted with a sound, soft cork, previously well dried and soaked in paraffine. Through this cork passed two glass tubes of about 5 mm. bore, one of which extended about two-thirds of the way to the bottom of the flask, and just above the cork was bent at right angles, the short projecting limb being some 20 mm. long. The other tube ended just below the cork on the inside of the flask, came out straight, and projected also about 20 mm. on the outside. Both were drawn down a little in diameter, about 5 mm. from the outside ends, so as to form a little socket for the small cork by which each tube was to be closed, insuring this cork coming to exactly the same position when inserted. The two small corks, the whole of the interior of the glass tubes, and so much of their exterior surface as was to be inside the flask were thoroughly protected by paraffine. The specific gravities of the glass, paraffine, platinum and paraffine-coated corks with tubes were taken at

[1]The dry acid in the gaseous state does not act upon glass, but, as it did not seem certain that, by the process used, perfect exclusion of moisture would be secured, it was thought better to take this precaution.

about the temperature to be used, and the figures obtained corrected for buoyancy in air by the formula—

$$G_r = G_a - \rho(G_a - 1)^1$$

From the thus corrected specific gravities, and careful weighings in air of observed temperature and pressure, the volumes and absolute weights *in vacuo* of all the materials concerned were deduced, save in the case of the hydrofluoric acid vapor itself, the volume of which was obtained by an actual calibration[2] of the part of the flask and tubes occupied by it.

As soon as the distillation of the acid and its collection in the leaden bottle was complete, the retort and capital were disconnected from the worm, and the upper end of the latter connected with the bent tube of the paraffine-lined flask, interposing in the first experiment another small flask, also protected by paraffine, and containing a little phosphorus pentoxide, as the means of removing any last traces of aqueous vapor. Removing the freezing mixture from about the leaden bottle, the latter was surrounded with water at 25° C., and the water surrounding the worm was brought to the same temperature, while the flask was at 1° or 2° lower. The hydrofluoric acid thus vaporized filled the whole apparatus, gradually expelling the air, and the excess escaped through a long India-rubber tube attached to the exit glass tube, and carried through a hole in the door-casing to the outside atmosphere, thus avoiding danger to the lungs and eyes, and risk of corrosion of the outside of the flask. When the escape of vapor slackened, the two tubes entering the flask were quickly disconnected from the rest of the apparatus and the little paraffine-soaked corks at once inserted. In doing this but one tube at a time was open, and that but for a moment.

The flask was then placed in a deep cylinder of sheet zinc, of diameter to just fit it, and this was immersed in a much larger cylinder, containing some 30 litres of water, at a little over 30° C., a cover with small openings in it being fitted over both. Previous experiment with a similar flask of air and enclosed thermometer

[1] G_r being the real specific gravity of the body, G_a the apparent specific gravity of same taken without air correction by simple weighings in air and water, and ρ the ratio of the densities of air and water under existing conditions of temperature and pressure.

[2] With water of known temperature, as the weight of mercury necessary would hardly have been safely borne by the flask.

showed what small allowance to make in the temperature of the water in order to bring the flask and its gaseous contents to the desired point. In the actual experiments with hydrofluoric acid a thermometer was placed on the upper part of the outside of the flask, while another was immersed in the water of the outer vessel. From time to time, as the temperature of the flask rose, the little cork was partly withdrawn for a moment from the straight vertical exit tube, and the surplus vapor was thus allowed to escape. In doing this one or two small, but bad, burns were made upon the fingers by the frightfully corrosive dry acid, of whose dangerous character one can hardly speak too strongly.

When the temperature of the flask had become stationary at or very close to 30° the little corks were firmly inserted in their seats, the flask was removed from the zinc cylinder, allowed to cool to the temperature of the balance-room, which had, however, been warmed up for several hours by a stove to a little over 25°, and was then accurately weighed.

The following result was obtained in the first experiment:

Weight of flask, etc., and vapor, *in vacuo*,	393.781 grams.
" " empty, "	386.531 "
Weight, *in vacuo*, of 4347.4 cc. of vapor at 29° C. and 743.7 mm. (cor.) = 3846 cc. at 0° C. and 760 mm.,	7.250 grams.

Hence, 1 liter of vapor at 0° and 760 mm. = 1.885 grams.
Hence, sp. gr. of vapor (H* = 1) = 21.06,
or molecular weight = 42.12.

As soon as the weighing was over the flask was washed out with distilled water enough to largely dilute the acid, into a platinum dish, and the purity of the liquid examined. It was quite clear and free from silicon or lead, and gave no reaction for sulphuric or sulphurous acid, but on testing with ammonium molybdate very distinct evidence was obtained of the presence of phosphoric acid. This had been suspected from the energy with which the phosphorus pentoxide, of which fortunately but little had been used. was attacked by the vapor. In all probability phosphorus pentafluoride had been formed and carried forward with the hydrofluoric acid. This may serve to account for the vapor density of the latter coming out somewhat too high for even the formula

*One liter of hydrogen at 0° and 760 mm. at Univ. of Va. = .089488 gram.

H_2F_2 (requiring sp. gr. = 20). Any traces of air or aqueous vapor which might have been present would, of course, have tended on the contrary to produce a lower result.

In order to avoid this ascertained source of error in a second experiment, the phosphorus pentoxide was omitted altogether, the upper end of the leaden worm was directly connected to the large flask, and as the means of finally drying the vapor, a little sulphuric acid of full strength (pure H_2SO_4—not SO_3) was added to the liquid hydrofluoric acid in the leaden bottle while it was still in the freezing mixture, before proceeding to vaporize the latter acid at the very moderate temperature of 25°. A new flask, lined with paraffine and fitted with tubes as before, was used, and the following result was obtained :

Weight of flask, etc., and vapor *in vacuo*, 428.255 grams.
" " empty " 421.436 "

Weight, *in vacuo*, of 4394.7 cc. of vapor
at 30.5° C. and 745.2 mm. (cor.) =
3876.5 cc. at 0° C. and 760 mm., 6.819 grams.
Hence, 1 litre of vapor at 0° and 760 mm. = 1.759 gram.
Hence. sp. gr. of vapor (H = 1) = 19.66,
or molecular weight = 39.32.

In this case the dilute acid washed out from the flask after the experiment seemed to be quite pure, or at any rate was free from silicon, lead, sulphuric and sulphurous acids. In both experiments the flask was, immediately after weighing, carefully inspected in a strong light, and no visible trace of liquid could be observed on the inside surface.

The glass, examined after removal of the paraffine, was found quite uninjured, except a slight trace of corrosion on the outside close to the exit.

The figures obtained obviously justify the assumption that at 30° C. the molecule of hydrofluoric acid vapor should be represented not as HF, but as H_2F_2, since the agreement with this assumption of the vapor density obtained in the two experiments is too close to be fairly accounted for by the mere general idea of imperfect gaseous condition, and it is certain that no such quantity of actually liquid acid as would be necessary to account for the double weight could possibly have escaped detection on the inner surface of the flask. At higher temperatures, such as those at

which Gore's measurements were made, dissociation manifestly takes place, leading to the production of diatomic molecules of HF.

The structure of the molecule of double weight, H_2F_2, may be well viewed as resulting from fluorine behaving not only as a monad but also as a triad, and acting in double atoms,

$$—F = F—,$$

like those of nitrogen,

$$—N = N—$$

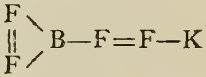
in the di-azo compounds. In such a condition the element presents a pseudo-dyad character, and becomes capable of replacing oxygen, and manifesting the *linking* function of the latter. Admitting, therefore, that the atomic weight of fluorine remains fixed at 19, we can see that the molecule of hydrofluoric acid may at high temperatures be H—F, analogous to that of hydrochloric acid, while at a little above the boiling point under ordinary pressure the structure may be H—F=F—H, and thus analogous to that of water.[1]

This assumption, supported by the experimental evidence now brought forward, serves conveniently to explain the constitution of a number of fluorine compounds, whose formulæ are difficult to write in a satisfactory way if fluorine be considered as exclusively monad.

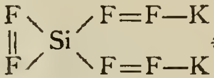
Thus we may view:

Potassium hydro-fluoride—KHF_2 as K—F=F—K

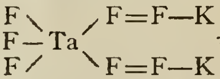
Potassium boro-fluoride—KBF_4 "



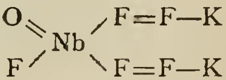
Potassium silico-fluoride—K_2SiF_6 " *



Potassium fluo-tantalate—K_2TaF_7 " †



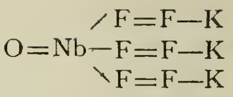
Potassium fluoxy-niobate—K_2NbF_5O as †

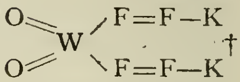


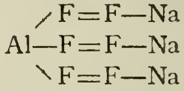
[1] Gore sums up the results of his numerous experiments on the chemical behavior of this interesting substance with the sentence: "From the various experiments already described, we may conclude that hydrofluoric acid is by its properties placed between hydrochloric acid and water, but is much more closely allied to the former than to the latter."

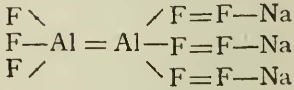
* On the type of a meta-silicate. Like formulæ apply to the analogous compounds of titanium, zirconium and tin.

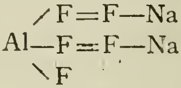
† Or these formulæ may be doubled, so as to correspond exactly with the oxygen pyro-tantalate and pyro-niobate.

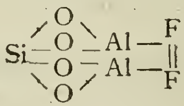
Potassium fluoxy-niobate — K_3NbF_6O as  *
(cuboid-Marignac)

Potassium fluoxy-tungstate—$K_2WF_4O_2$ as  †

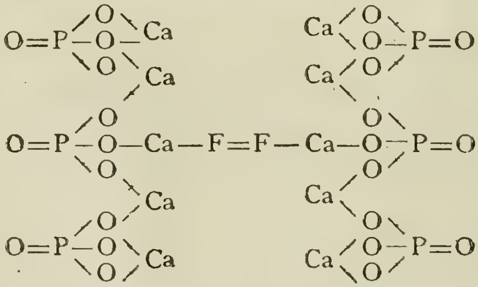
Cryolite Na_3AlF_6 " 

Chiolite $Na_3Al_2F_9$ " 

Chodneffite Na_2AlF_5 " 

Topaz $Al_2SiF_2O_4$ "  ‡

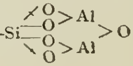
Apatite—$Ca_5P_3FO_{12}$—might be written:

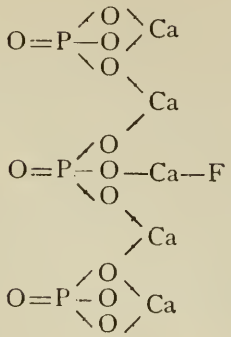


but, in view of the replacement of fluorine by chlorine in this mineral, as in the analogous pyromorphite and mimetite, it is doubtless better, as well as simpler, to suppose the molecule to be merely—

* On the type of an ortho-niobate.

† As for the normal tungstate. The case of the fluoxy-molybdate is of course the same.

‡ Like Andalusite—Al_2SiO_5— 



UNIVERSITY OF VIRGINIA, *April* 26, 1881.

Laboratory Notes from the University of Cincinnati.

XX.—SOME DOUBLE AND TRIPLE OXALATES CONTAINING CHROMIUM.

By F. W. CLARKE.

Chromic oxalate unites with other oxalates to form two well known series of double salts. One series is represented by the blue potassio-chromic oxalate, $Cr_2K_6C_{12}O_{24}6H_2O$. The other is typified by the red salt, $Cr_2K_2C_8O_{16}8H_2O$. The compounds described in this paper belong to the higher series.

The barium, strontium, and calcium salts of this series were discovered by Rees-Reece.[1] By mixing solutions of the ammonium salt with the chlorides of barium, strontium, and calcium, he obtained precipitates of dark violet silky needles, having the following formulæ :

1. $Cr_2Ba_3C_{12}O_{24}.12H_2O$.
2. $Cr_2Ba_3C_{12}O_{24}.18H_2O$.
3. $Cr_2Sr_3C_{12}G_{24}.18H_2O$.
4. $Cr_2Ca_3C_{12}O_{24}.36H_2O$.

By a different process, Berlin[2] prepared a calcium salt with 18 aq., a lead salt with 15 aq., and a silver salt with 9 aq.; besides other compounds which need no mention here.

[1]Compt. Rend. **21**, 1116. [2]Berzelius' Jahresbericht, **24**, 244.

About a year ago I requested Mr. E. A. Kebler to reprepare the barium salts described by Rees-Reece. The only variation from the method of the latter chemist was in using the potassium salt instead of the ammonium salt for the precipitant. Masses of very dark green silky needles were thrown down, and these were easily recrystallizable from boiling water. Two hydrates of the desired salt were thus obtained, one agreeing with the twelve molecule salt of Rees-Reece, while the other, lighter colored, contained but seven molecules of water. For the latter, the subjoined analytical data were found:

	Found.	Theory.
Cr	8.94	8.90
Ba	34.96	35.16
H_2O	10.91	10.77

The formation of this new hydrate naturally led to experiments aimed at the discovery of the conditions under which different degrees of hydration were produced. Although this point was not definitely settled, interesting results were secured. Four samples of the double oxalate were precipitated, two from dilute and two from concentrated solutions. Two were thrown down in the cold, and two were precipitated boiling. All the precipitates were in the form of green silky needles, which were carefully air dried. In these several preparations the following percentages of water were obtained:

Precip. concent'd, cold	9.50	9.78	9.19			Mean	9.49
" " hot	9.39	9.31				"	9.35
" dilute, cold	9.98	9.90	9.43	10.10	10.72	"	10.03
" " hot	12.07	12.13	11.12			"	11.77

Theory for 6 molecules of water	9.38
" " 7 " "	10.77
" " 8 " "	12.13

It will be seen that the two salts precipitated from concentrated solutions are definitely hexhydrated; the third salt gave doubtful results; while the last agrees fairly with the percentage for eight molecules of water. Evidently the six molecule salt is definite and typical; doubtless the twelve and eighteen molecule salts of Rees-Reece are definite also; all the other hydrates may be but mixtures of the lowest with one of the higher compounds. This point

remains to be settled. The color is always darker, the higher the hydration; but, though green under ordinary circumstances, all the salts described in this paper become dull violet by gaslight. Specific gravities were found as follows:

$Cr_2Ba_3C_{12}O_{24}$	Anhydrous	2.570 at 6 8°
"	$6H_2O$.	2.445 at 13.9°
"	$12H_2O$.	2.372 at 27°.

Here the second salt is nearly a mean between the other two.

The strontium salts were also prepared by Mr. Kebler, under varying conditions of temperature and dilution. These too came down as pale green satiny needles of considerable beauty, and easily recrystallizable from hot water. From cold dilute solutions the salt $Cr_2Sr_3C_{12}O_{24}.12H_2O$ was precipitated.

	Found.	Theory.
Cr	9.36	9.37
Sr	23.59	23.64
H_2O	19.29	19.45

From the mother liquor and washings of this salt a somewhat lower hydrate was deposited, possibly a mixture, corresponding in hydration to 10½ molecules of water. Specific gravity 2.148 at 8.8°. From hot concentrated solutions of the precipitants a decahydrated salt was obtained. Calling these salts A and B respectively, we have the following analytical data:

	Found.		Theory 10½ aq.	Theory 10 aq.
	A.	B.	A.	B.
Cr	9.55	9.52	9 59	9.67
Sr	24.14	24.31	24.22	24.45
H_2O	17.36	16.87	17.40	16.75

I am inclined to look upon these preparations as mixtures of the twelve molecule salt with small quantities of a hexhydrated salt yet to be discovered.

The mother liquors from all these strontium precipitates were united and concentrated. Upon standing, a very dark green, almost black, crystalline crust was deposited. This, which had a specific gravity of 2.155 at 12.8°, proved to be a new triple oxalate having the formula $Cr_2Sr_2K_2C_{12}O_{24}$, with either eleven or twelve molecules of water.

	Found.	Theory, 11 aq.	Theory, 12 aq.
Cr	9.51	9.60	9.44
Sr	16.15	16.15	15.89
K	7.26	7.22	7.10
H_2O	18.33	18.28	19.61

I suspect that the twelve molecule formula is the true one, and that the salt as analyzed by Mr. Kebler may have been slightly effloresced. Still, the analytical agreement with the lower formula is wonderfully close.

The discovery of this new triple salt led to a search for the corresponding barium compound. The ordinary bario-chromic oxalate was accordingly dissolved with an equivalent quantity of the potassium salt in boiling water, and the mixture was then heated with barium carbonate in order to remove a little free oxalic acid which happened to be present as an impurity. Upon filtering, dull bluish green needles were deposited, having the composition $Cr_2Ba_2K_2C_{12}O_{24}$, with five or six molecules of water.

	Found.	Theory, 5 aq.	Theory, 6 aq.
Cr	9.86	9.68	9.53
Ba	24.25	25.51	25.09
K	7.41	7.28	7.14
H_2O	8.65	8.38	9.89

Since the salts which yield this triple salt each contained six molecules of water, I am inclined to consider that as the true degree of hydration for the compound now in question. In fact, throughout this series of complex oxalates, the hydration is almost uniformly six molecular, or represented by some even multiple of six. The chief exceptions are the lead and silver salts of Berlin, with 15 aq. and 9 aq. respectively; values which are regular submultiples of six.

The process by which these barium and strontium salts are prepared from the potassium salt is suggestive of their constitution. We may fairly regard the chromic oxalate itself as a weak acid, having the subjoined structural formula:

$$\left.\begin{matrix} H.C_2O_4 \\ H.C_2O_4 \\ H.C_2O_4 \end{matrix}\right\} Cr—Cr \left\{\begin{matrix} C_2O_4.H. \\ C_2O_4.H. \\ C_2O_4.H. \end{matrix}\right.$$

These six atoms of hydrogen are replaceable by six potassium atoms, by three barium atoms, or by two of each, and so on with

all the other salts of the series. If chromium be regarded as trivalent, the formulæ should of course be halved.

We attempted to prepare the sexbasic acid here suggested, but did not attain to final results. The barium salt was decomposed by an exactly equivalent quantity of sulphuric acid. Upon filtering, an acid liquid was obtained, strongly dichroic, and dark violet red by transmitted light. Probably this was the acid in question, but actual proof is yet wanting.

Mr. Kebler also tried to prepare several other salts of the series under discussion, but unsuccessfully. No calcium salt like that of Rees-Reece could be obtained. Calcium oxalate, slightly discolored by chromium, was thrown down every time. With salts of cadmium, cobalt, ferrous iron, zinc, copper, lead, and stannous tin, the blue potassio-chromic oxalate gives cither no precipitate, or else, after some time, a precipitate of the ordinary oxalates of the metals in question. The filtrates from these oxalates afterwards deposit crystals, too impure for analysis, which appear to be the potassio-chromic salt of the red series. The plan of heating bario-chromic oxalate with the sulphates of cadmium, cobalt, copper, iron, and zinc was also tried. In each case an ordinary oxalate was formed, mixed with barium sulphate.

XXI.—THE TITRATION OF TARTARIC, MALIC AND CITRIC ACIDS WITH POTASSIUM PERMANGANATE—PRELIMINARY NOTE.

COMMUNICATED BY F. W. CLARKE.

Some time ago, in the course of certain investigations upon the tartrates of antimony, it occurred to me that tartaric acid, like oxalic acid, might perhaps be conveniently titrated with potassium permanganate. A single qualitative experiment showed that a fair end reaction was attainable, and the same thing proved to be true of malic and citric acids also. Accordingly I put the question into the hands of Mr. Miles Beamer, who made the following determinations:

The titrations were performed in all essential particulars exactly as for oxalic acid. A solution was prepared containing a definite

quantity of tartaric acid, and upon this the permanganate solution, which was approximately twentieth normal, was standardized. Sulphuric acid was of course added before titrating. The color changes were rather slower than with oxalic acid, and required a somewhat higher temperature. They were also possibly a trifle less delicate, but still fairly concordant results were easily obtained.

Having standardized the permanganate solution, it was used for estimating the percentage of tartaric acid in sodium potassium tartrate, $C_4H_4KNaO_6 4H_2O$. The following was the result, reckoning the acid as $C_4H_4O_6$:

Percentage found,	51.63
" theoretical,	52.48
Error,	0.85

As this percentage was rather roughly determined, a fresh experiment was made, with a new and more carefully standardized permanganate solution.

$C_4H_4O_6$ found,	52.75
Error,	0.27

Two sets of titrations were also made upon hydrogen potassium tartrate, $C_4H_5KO_6$. The percentages of acid, reckoned as $C_4H_5O_6$, came out as follows:

First set,	79.20
Second, "	78.88
Theory,	79.25

Tartar emetic was treated as follows: Its solution was mixed with a slight excess of ammonium sulphide, and then acidulated with dilute sulphuric acid. By warming and filtration, all the antimony was thus removed, and the tartaric acid was left in a suitable condition to be determined. The salt used, however, was found to have lost some of its crystalline water, so that the results were not comparable with theory. Other determinations are now in progress upon certain tartrates of antimony, and will be published in due time.

The experiments upon malic acid precisely resembled those upon tartaric acid, and were conducted by Mr. C. S. Evans. As we had no definite malates at hand, a standardized solution of malic acid was neutralized partly with caustic soda and partly with am-

monia. Thus solutions of alkaline malates were obtained containing known quantities of acid. Upon titrating these solutions, it was found that they behaved exactly like the acid itself. The ammonium malate gave 99.89 per cent. of the acid known to be present, while the sodium salt gave 100.007 per cent.

With citric acid the results are still very incomplete. Mr. L. R. Freeman standardized a solution of permanganate upon this acid, and found the final reaction to be fairly sharp, but very slow towards the end. This standard permanganate, applied to an analysis of trisodium citrate, gave in mean 53.36 per cent. of acid, reckoned as $C_6H_5O_7$. The theoretical amount should be 52.94. Error, 0.42. Mr. Evans attempted a repetition of these experiments, but, for some unknown reason, was not successful.

These preliminary figures show fairly well that the permanganate solution is suited to the titrations in question. The results may not be as sharp as with oxalic acid, but still they are fairly good. Some comparative titrations by Mr. Freeman show that tartaric and malic acids are oxidized to carbonic acid and water, while with citric acid the result is, of course, more complex. Although, then, it may be possible to standardize the permanganate upon oxalic acid once for all, I suspect it is better to standardize it directly upon whichever acid is actually to be estimated. I hope that either Mr. Beamer or myself will be able soon to present some additional figures.

XXII.—RELATION BETWEEN TEMPERATURE AND THE RATE OF CHEMICAL ACTION.

By R. B. Warder.

The speed of the reaction,

$$C_2H_5.O.C_2H_3O + NaOH = NaC_2H_3O_2 + C_2H_5OH,$$

in dilute aqueous solution, has been observed at temperatures from 3.6° to 37.7°C. This series of determinations nearly agrees with the equilateral hyperbola,

$$(7.5+a)\,(62.5°-t)=521.4,$$

where t is the temperature, and a expresses the number of gram-

equivalents per liter which would (according to the theory of the action of mass) react upon each other per minute in a solution kept of normal strength.

Further details are deferred to another number.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

IX.—OXIDATION OF SULPHAMINEMETATOLUIC ACID IN ALKALINE AND IN ACID SOLUTION.

By R. D. Coale and Ira Remsen.

In a paper entitled "Experiments in the Para-series,"[1] it has been shown that, when sulphamineparatoluic acid is oxidized with potassium permanganate in alkaline solution, it is transformed into the peculiar anhydride of sulphamineterephthalic acid called terephthalic sulphinide; whereas, when the oxidation is conducted in acid solution, the product is sulphoterephthalic acid. These results led to the examination of sulphaminemetatoluic acid—an examination which was particularly desirable, as a dispute had arisen in regard to the nature of the product formed when the acid mentioned is oxidized. One of us has repeatedly stated that the product formed when the free acid is treated with permanganate is sulphoisophthalic acid, while our opponent persistently denies this statement, and claims that the product is sulphamineisophthalic acid. In this paper it is shown that both of these acids, or at least the former and the anhydride of the latter, may be obtained at will, as readily as the corresponding para-compounds. To prove further that the substance obtained by oxidation in acid solution is in reality sulphoisophthalic acid, the latter has been prepared from xylenesulphonic acid directly, without the intermediate preparation of nitrogenous compounds. The results here recorded furnish a complete and final answer to the statements of our opponent above referred to, and they can

[1] This Journal, 2, 50.

leave no room for doubt regarding the accuracy of the statements already made by one of us in earlier papers of this series.

New Experiments on the Oxidation of Xylenesulphamides.

In the first paper of this series the oxidation of the amides of xylenesulphonic acids was fully discussed. As, however, in the course of the present investigation we have had occasion to oxidize large quantities of these amides, we have gained some new experience, the results of which are here briefly recorded. As regards the preparation of the amides, nothing need be added to the earlier statements. The separation was not carried to completion, and, indeed, without any separation a perfectly pure oxidation product may readily be obtained. At first, the partly purified amide was treated with the pyrochromate mixture, as directed in the first paper. In order to hasten the preparation of the acid, six hundred grams of the amide were divided into six equal portions, and each portion brought into a separate flask with the necessary quantity of the oxidizing mixture, no special precautions being taken in heating the flasks. The result of this was that scarcely a trace of the desired acid was obtained from each hundred grams of amide. The oxidation took place violently and the amide was almost completely destroyed. This brings to mind very vividly the first experiment performed in the oxidation of these amides, in which the same result led to the natural but erroneous conclusion that the amide which formed the principal bulk of the mixture used can not yield an acid by oxidation. In order to get the acid, it is necessary to go to work cautiously. Smaller quantities than those above mentioned should be taken, and, in heating, certain precautions must also be observed. As the result of a large number of experiments undertaken with the distinct object of determining the best conditions, we give the following specific directions for the oxidation of α-xylenesulphamide: The oxidizing mixture consists of 141 grams of potassium pyrochromate and 213 grams of ordinary concentrated sulphuric acid, diluted with three times its volume of water. After the mixture is cooled to the temperature of the air, 22 grams of the amide are added. The whole is then gently heated on the water-bath until the effervescence which indicates the beginning of the oxidizing action is seen. The flask is then connected with an inverted condenser, and the contents kept quietly

boiling for about an hour by means of a small free flame. The mixture is allowed to cool, and the oxidation product crystallizes out. The separation of this product from the little amide which remains unchanged is effected as described in the first paper already referred to. This unchanged amide is *remarkably pure α-amide*, which shows that the β-amide is completely destroyed, as has repeatedly been claimed. In the course of our work we obtained 85 grams of crude sulphaminemetatoluic acid, and this by recrystallization yielded 65 grams of finely crystallized pure acid. We examined the product with the greatest care with reference to the possible formation of an isomeric acid derived from the β-amide, but were unable to obtain the slightest evidence of the formation of such a substance. We may then unhesitatingly reaffirm the first statement that when a mixture of the α- and β-amides of xylenesulphonic acids is oxidized with chromic acid the β-amide is destroyed, while the α-amide yields a monobasic acid—sulphaminemetatoluic acid.

Oxidation in Acid Solution.

It has already been shown that when free sulphaminemetatoluic acid is treated with potassium permanganate, the product which is obtained in the form of the acid potassium salt is sulphoisophthalic acid. This salt is very easily obtained in perfectly pure condition, giving no evidence of the presence of nitrogen when tested according to Lassaigne's well-known method. In order to gain a more thorough knowledge of the tribasic sulphonic acid, a number of its salts were prepared and examined.

The starting point for the preparation of the salts was the acid potassium salt first obtained. As regards this salt, the only new fact to be recorded is that a determination of its solubility in water made according to the method devised by Victor Meyer, showed that 1.59 parts of the salt are soluble in 100 parts of water at 26°.

Neutral potassium sulphoisophthalate, $C_6H_3 \begin{cases} SO_3K \\ CO_2K \\ CO_2K \end{cases}$.

This was obtained by exactly neutralizing a solution of the primary salt by means of a solution of potassium carbonate, and then evaporating to dryness. It is very easily soluble in water, and could not be made to crystallize. The results of the analysis, though

not satisfactory, show that the salt contains three atoms of potassium in the molecule.

0.2085 gram dried salt gave 0.1412 gram K_2SO_4.

Calculated.	Found.
32.56	30.40

An attempt was made to prepare the *secondary potassium salt*, $C_6H_3\begin{cases} SO_3K \\ CO_2K \\ CO_2H \end{cases}$, by dividing a solution of the primary salt into two equal parts, exactly neutralizing one-half with potassium carbonate and then bringing the two together. The solution was then evaporated, and a crystalline deposit obtained. This was found not to have a uniform composition. A similar result was reached by Remsen and Burney[1] in attempting to prepare the corresponding salt of sulphoterephthalic acid.

The *secondary barium salt*, $C_6H_3\begin{cases} \left.\begin{matrix} SO_3 \\ CO_2 \end{matrix}\right\} Ba + xH_2O, \\ CO_2H \end{cases}$ is the one originally obtained by Remsen and Iles.[2] We have found that the amount of water of crystallization which it contained varies, according to the conditions, from 1 to 2 molecules, and it appears from a single observation made on the same salt prepared in another way that it may contain even as much as 4 molecules. When the salt is prepared in the usual way by adding a solution of barium chloride to a boiling solution of the primary potassium salt, and then allowing the whole to cool, it contains 6.62 per cent. water, an amount which corresponds to $1\frac{1}{2}$ molecules. This was clearly shown by a number of analyses made in the first part of the investigation, and the results have been confirmed by us. If, however, the solution of the primary potassium salt be rather dilute, and only *warm* when the barium chloride is added, then the barium salt takes a much longer time to crystallize out, and is obtained in larger crystals, which contain 8.63 per cent. of water. This indicates the presence of 2 molecules of water of crystallization. If the salt containing either $1\frac{1}{2}$ or 2 molecules of water be kept in boiling water for a time, it loses its crystalline form to a great extent, and then contains but 4.51 per cent. of water, corresponding to 1 molecule.

The analyses here given show the variation in the amount of water of crystallization of the barium salt prepared at different temperatures.

[1] This Journal, 2, 409. [2] Ibid. 1, 126.

1. Salt prepared by adding barium chloride to a boiling solution of the primary potassium salt. 0.2067 gram salt lost 0.0137 gram H_2O at 212°.

Calculated for $1\frac{1}{2}H_2O$.	Found.
6.62	6.63

2. Salt prepared by adding barium chloride to a *warm, dilute solution* of the primary potassium salt. 0.2020 gram salt lost 0.0176 gram H_2O at 215°.

Calculated for $2H_2O$.	Found.
8.63	8.71

3. Salt after being in boiling water for a time. 0.2042 gram salt lost 0.0103 gram H_2O at 220°.

Calculated for $1H_2O$.	Found.
4.51	5.04

A determination of the solubility showed that only 0.071 part dissolves in 100 parts of water at 23.5°.

Primary barium salt, $\left(C_6H_3\begin{cases}SO_3\\CO_2H\\CO_2H\end{cases}\right)_2Ba$. The attempt to prepare this salt proved unsuccessful. The secondary salt dissolves readily in hydrochloric acid and probably the primary salt is in the solution, but we were unable to get it out in pure form, the composition of the product varying considerably.

Neutral barium sulphoisophthalate, $\left(C_6H_3\begin{cases}SO_3\\CO_2\\CO_2\end{cases}\right)_2Ba_3 + 3H_2O$. This was prepared by boiling the secondary salt and barium carbonate together in water. On filtering and evaporating, a deposit was obtained which did not present a uniform appearance. The salt seemed to undergo some decomposition when its solution was evaporated. The character of the decomposition we have not, however, discovered. The deposit was analyzed with these results:

I. 0.2383 gram salt lost 0.0134 gram H_2O at 195° and gave 0.1711 gram $BaSO_4$.

II. 0.2069 gram salt gave 0.1484 gram $BaSO_4$.

	Calculated.	Found. I.	Found. II.
$3H_2O$	5.68	5.62	...
Ba_3	43.22	42.22	42.17

By boiling the secondary barium salt with sulphuric acid, filtering and evaporating to dryness, *free sulphoisophthalic acid* was obtained. It is very easily soluble in water and hygroscopic. After standing for several days over sulphuric acid it was obtained as a semi-crystalline mass fusing at 243-244° (uncorr.). In the paper already referred to the fusing point of the acid is stated to be 285–287°. This must be an error. It is possible that in some of the earlier preparations the sulphamineisophthalic acid may have been obtained, and that this may have been the substance used in making the original determinations, as at that time it was not known that both the non nitrogenous and the nitrogenous acids may be obtained by oxidation of sulphaminemetatoluic acid.

The existence of the salts above described, notwithstanding their unattractive properties, serves to show, at least, that the acid from which they are derived is tribasic; and when the descriptions of these salts are compared with those of the salts of sulphamineisophthalic acid, as will be done below, it will be seen that there is no possibility of confounding the two series of compounds.

Oxidation in Alkaline Solution.

Remsen and Hall[1] have shown that the addition of an alkali to the oxidizing mixture in the case of sulphaminemetatoluic acid causes the formation of terephthalic sulphinide. We have obtained a similar result with the meta acid.[2] The acid was treated with the oxidizing mixture in these proportions: 5 grams acid, 20 grams potassium permanganate, water 190 cc., and 10 cc. caustic potassa containing 2.3 grams potassium hydroxide, or an excess of one gram above the amount required for the neutralization of the acid.

The mixture was heated for five or six hours on the water-bath; the reduction completed by means of a few drops of alcohol; the solution filtered and evaporated to a small volume. Hydrochloric acid was now added, and on cooling the product crystallized out. One recrystallization is usually sufficient to purify it. The substance thus obtained crystallizes well, and fuses at 282.5° (uncorr.). Lassaigne's test shows the presence of nitrogen without difficulty. The analyses proved that the substance is anhydrosulphamineisophthalic acid or *isophthalic sulphinide.*

[1] This Journal, **2**, 132.

[2] Berichte der deutsch. chem. Gesell. **12**, 1436.

Calculated for $C_6H_3\begin{cases}SO_2\\CONH\\CO_2H\end{cases}$.		Found. I.	II.
S ...	14.09	14.41	14.34
N ...	6.14	6.50	6.34

Mono-potassium anhydrosulphamineisophthalate, $C_6H_3\begin{cases}SO_2\\CONH\\CO_2K\end{cases} + 2H_2O$. This salt was prepared by adding the required amount of potassium carbonate in solution to a solution of the sulphinide. The solution was then evaporated to a small volume, and, on cooling, the salt crystallized out. It crystallizes in well formed, transparent, rectangular prisms, which lose their water of crystallization at 110–120°. The analyses gave these results:

Calculated for $C_6H_3\begin{cases}SO_2\\CONH\\CO_2K\end{cases} + 2H_2O$.		Found. I.	II.
K ...	12.99	12.93	12.96
$2H_2O$ ...	11.92	11.89	11.80

To establish the bibasicity of the acid, neutralization experiments were made with the results here stated. Two portions of the acid potassium salt were treated with a standard solution of ammonia. On the assumption that the acid is bibasic, the quantities of the standard ammonia solution calculated as compared with the quantities used are as follows:

	Calculated.	Used.
I.	5.8 cc.	5.76 cc.
II.	5.5 cc.	5.54 cc.

2.3 parts of the salt are soluble in 100 parts of water at 26.3°.

Neutral potassium sulphamineisophthalate, $C_6H_3\begin{cases}SO_2NH_2\\CO_2K\\CO_2K\end{cases} + 4H_2O$. This was prepared by exactly neutralizing the acid potassium salt. On evaporating almost to dryness and cooling, the salt crystallized in long needles, but owing to its extreme solubility it could not be obtained dry in good crystals. Analyses were made with these results.

I. 0.204 gram salt lost 0.0381 gram H_2O at 120°, and gave 0.0938 gram K_2SO_4.

II. 0.2100 gram salt lost 0.0377 gram H_2O at 130°, and gave 0.0986 gram K_2SO_4.

Calculated for $C_6H_3\left\{\begin{array}{l}SO_2NH_2\\CO_2K+4H_2O.\\CO_2K\end{array}\right.$		Found. I.	II.
K_2	19.88	20.64	21.07
$4H_2O$	18.31	18.68	17.95

Acid calcium anhydrosulphamineisophthalate, $\left(C_6H_3\left\{\begin{array}{l}SO_2-\\CONH\\CO_2\end{array}\right.\right)_2$ $Ca+xH_2O$. This was prepared by dividing a solution of the free acid into two parts, neutralizing one-half and then bringing the two together. On evaporating to a small volume, the salt separated partly in amorphous form and partly in feather-shaped crystalline masses. It loses water rapidly, so that no accurate determination of the entire amount of water of crystallization first contained in the salt can be made. Dried in the air it contains 4 molecules, which are given off at 150°. The analyses here recorded prove the composition of the salt.

I. 0.2143 gram salt lost 0.0263 gram H_2O at 150°, and gave 0.0522 gram $CaSO_4$.

II. 0.2276 gram salt lost 0.0286 gram H_2O at 150°, and gave 0.0553 gram $CaSO_4$.

	Calculated.	Found. I.	II.
Ca	7.09	7.16	7.15
$4H_2O$	12.77	12.27	12.57

Calcium sulphamineisophthalate, $C_6H_3\left\{\begin{array}{l}SO_2NH_2\\ \left.\begin{array}{l}CO_2\\CO_2\end{array}\right\}Ca+6H_2O,\end{array}\right.$ was obtained by boiling a solution of the acid with finely powdered Iceland spar. On evaporating to a small volume it crystallizes out in large, finely developed apparently monoclinic crystals. These crystals rapidly lose three molecules of their water of crystallization on exposure to the air, and this loss is accompanied by a complete transformation of the crystals. They become opaque and fall to pieces, forming an amorphous powder. This powder, however, still contains 3 molecules of water which are not given off below 170–180°.

The crystals first obtained gave these results:

0.4214 gram salt lost 0.1181 gram H_2O at 180°, and gave 0.1531 gram $CaSO_4$.

	Calculated.	Found.
Ca	10.23	10.68
$6H_2O$	27.62	28.03

The results obtained in the analysis of the air-dried salt are as follows:

0.2004 gram salt lost 0.0341 gram H_2O at 190°, and gave 0.0806 gram $CaSO_4$.

	Calculated.	Found.
Ca	11.87	11.83
$3H_2O$	16.02	17.02

Acid barium anhydrosulphamineisophthalate, $\left(C_6H_3\left\{\begin{array}{l}SO_2\text{—}\\ CONH\\ CO_2\end{array}\right.\right)_2$ $Ba+4H_2O$. To obtain this salt the most convenient method is to boil a solution of the acid potassium salt with barium chloride. This is also the method best adapted to the preparation of the acid barium salt of sulphoisophthalic acid. In the latter case, however, a precipitate is produced almost instantly, and very violent "bumping" is produced; while in the former case no precipitate is formed, and the clear liquid boils quietly. On cooling, if the solution be sufficiently concentrated, the acid barium salt crystallizes out in well formed, transparent, monoclinic plates, which lose their water of crystallization at 100–105°. The analysis gave the accompanying results:

0.1777 gram salt lost 0.0201 gram H_2O at 110°, and gave 0.0625 gram $BaSO_4$.

	Calculated.	Found.
Ba	20.68	20.72
$4H_2O$	10.89	11.31

Barium sulphamineisophthalate, $C_6H_3\left\{\begin{array}{l}SO_2NH_2\\ \left.\begin{array}{l}CO_2\\ CO_2\end{array}\right\}Ba\end{array}\right.+4H_2O$, was prepared by boiling the acid with barium carbonate in a large volume of water, as the salt is difficultly soluble. It is obtained in large, well formed, thick monoclinic plates, which lose part of their water of crystallization when exposed to the air, become opaque and fall to pieces. If a solution of the salt be boiled, a

white powder is deposited, a partial decomposition apparently taking place. In the crystallized form the salt contains 4 molecules of water of crystallization. A rapid determination gave 16.28 per cent. water, while 15.93 per cent. are required for $4H_2O$. The air-dried salt contains varying amounts of water, and analyses were therefore made of the salt dried at 130°.

0.2215 gram salt gave 0.1365 gram $BaSO_4$.

	Calculated.	Found.
Ba	36.21	36.23.

From the descriptions of the salts derived from sulphoisophthalic acid and from sulphamineisophthalic acid, it will be seen that there is very little resemblance between the corresponding members of the two series. In general, the salts of the latter acid are more easily prepared, and have better properties than those of the sulphonic acid. The difficulties met with in the preparation of the neutral salts of the tribasic sulphonic acid suggest the experiences in connection with sulphoterephthalic acid already recorded, but the results obtained with both these acids leave no room for doubt that they are really *tribasic*. Since the publication of the paper on sulphoterephthalic acid, P. Schoop[1] has stated that owing to the impossibility of obtaining neutral salts of sulphoterephthalic acid, prepared by treating terephthalic acid with "solid sulphuric acid," the sulphonic acid must be regarded as *bibasic*. This conclusion certainly does not apply to the sulphonic acid previously described, and it is difficult to see how two sulphoterephthalic acids can be formed, though, of course, two *may* be possible.

As a result of the experiments treated of in this paper, it will be seen that when sulphaminemetatoluic acid, $C_6H_3\begin{cases}SO_2NH_2\\CH_3\\CO_2H\end{cases}$ is oxidized in acid solution, *i. e.* when the free acid is oxidized, without the addition of an alkali, with potassium permanganate, the product is *sulphoisophthalic acid*, $C_6H_3\begin{cases}SO_2OH\\CO_2H.\\CO_2H\end{cases}$ Whereas, if a quantity of alkali but slightly in excess of that required to neutralize the acid be added, and the oxidation be carried on otherwise in exactly the same way as in the first experiment, the product is *isophthalic sulphinide*, $C_6H_3\begin{cases}SO_2\rceil\\CO\ NH\\CO_2H.\end{cases}$

[1] Berichte d. deutsch. chem. Gesell. **14**, 223.

Sulphoisophthalic Acid from Metaxylenesulphonic Acid.

To make the proof concerning the nature of the substance called sulphoisophthalic acid complete, metaxylenesulphonic acid itself was oxidized, and the tribasic acid thus formed compared with that obtained by oxidizing sulphaminemetatoluic acid.

The potassium salts of the crude mixture of xylenesulphonic acids obtained by direct treatment of purified commercial xylene with sulphuric acid were subjected to oxidation in two stages, potassium pyrochromate being first used and then permanganate, as was done in the experiments with paraxylene and cymene. Though no special experiments have been performed with reference to this point, it appears from the observations here made that the permanganate acts most readily on the oxidizable groups situated in the ortho-position ; so that, if an ortho- and a para-group, or an ortho- and a meta-group be present together in the compound, the action first takes place in the ortho-group, and there seems to be considerable difficulty in effecting the oxidation of the other groups without complete decomposition of the compound. At all events, we have always obtained much more satisfactory results by oxidizing first with chromic acid, the action of which goes no farther than the para- and meta-groups, the ortho-group being unacted upon ; and then effecting the oxidation of the latter with permanganate. The yield was in no case satisfactory, but still we obtained enough of the product to enable us to make the desired comparison. The details of the process were the same as those described in the paper by Remsen and Kuhara,[1] and they need not here be repeated. An acid potassium salt was obtained, which in every respect resembles the acid potassium salt obtained by oxidation of sulphaminemetatoluic acid in acid solution. The analysis shows that the salt also has the same composition, $C_6H_3\begin{cases} SO_3K \\ CO_2H \\ CO_2H \end{cases} + 2H_2O$.

0.2059 gram salt lost 0.0230 gram H_2O at 140° and gave 0.0568 gram K_2SO_4.

	Calculated.	Found.
K	12.21	12.38
$2H_2O$	11.25	11.17

[1] This Journal, 2, 413.

On boiling a solution of this salt with barium chloride, all the characteristic phenomena observed in connection with the acid potassium salt first described were repeated. The precipitate was readily formed, and at once the most violent "bumping" began. The barium salt thus obtained proved to be secondary barium sulphoisophthalate, as was expected. Variations in the amount of water of crystallization contained in the salt prepared under different conditions were observed in this case as well as in that described in the earlier part of this paper. Indeed, in one preparation as much as 4 molecules of water were found, but, though attempts were made to obtain this salt a second time, they were unsuccessful. The properties of the salt were in every respect identical with those of the same salt prepared from the sulphamine acid.

A solubility determination showed that 0.075 parts dissolve in 100 parts of water at 23.5°. A similar determination with the salt first obtained showed that 0.071 parts dissolve in 100 parts water.

The analyses gave these results:

1. Salt prepared by adding barium chloride to a cold solution of the acid potassium salt.

I. 0.2042 gram salt lost 0.0306 gram H_2O at 218° and gave 0.1055 gram $BaSO_4$.

II. 0.2011 gram salt lost 0.0299 gram H_2O at 218° and gave 0.1043 gram $BaSO_4$.

Calculated for $C_6H_3\left\{\begin{array}{l}SO_3\\CO_2\\CO_2H\end{array}\right.\!\!\left.\begin{array}{l}\\\end{array}\right\}Ba + 4H_2O$.		Found. I.	Found. II.
Ba	30.24	30.38	30.50
$4H_2O$	15.85	14.99	14.87

2. Salt prepared from a warm solution:

0.2008 gram salt lost 0.0172 gram H_2O at 225°.

Calculated for $2H_2O$.	Found.
8.63	8.57

3. Salt boiled under water:

0.2042 gram salt lost 0.0103 gram H_2O at 220°.

Calculated for $1H_2O$.	Found.
4.51	5.04

The acid here described as obtained by the oxidation of metaxylenesulphonic acid has also recently been described elsewhere.

This description[1] agrees in the main with ours. The only difference observed is in the amount of water of crystallization in the acid barium salt. In the paper referred to it is stated that the salt contains three molecules of water. We have never analyzed a specimen containing this amount, but as the amount present is, to some extent, a matter of accident, it is very possible that under some circumstances a salt containing three molecules may be met with.

There can then be no doubt that the substance formed when sulphaminemetatoluic acid is oxidized in acid solution is in reality sulphoisophthalic acid, as has constantly been claimed by one of us. With this communication we may certainly regard the discussion in regard to the nature of the substance, as definitely concluded.

X.—CONCERNING MESITYLENIC SULPHINIDE.

By Ira Remsen and P. H. Broun.

At the conclusion of a paper on "Experiments with Mesitylene,"[2] an account of some unfinished experiments was given, which were undertaken with the object of determining the nature of the product formed by treating mesitylenesulphamide with chromic acid. These experiments have been continued by us and have led to the desired object. It will be remembered that when mesitylenesulphamide is treated with the ordinary chromic acid oxidizing mixture, only one of the three methyl groups contained in the compound is converted into carboxyl. It was at first believed that this result could be explained by the assumption that the substituting group exerts a protective influence on two of the methyl groups, with reference to which it occupies the ortho-position, while not interfering with the oxidation of the one methyl in the para-position. This conclusion was supported by analogy; and since the subject was first taken up in this laboratory, a number of cases have been added to those upon which the general idea of protection from oxidation is based. It is coming to be generally recognized that the law first enunciated in these papers, and which lies at the bottom of the transformations discussed in them, is valid; and if the

[1] Berichte d. deutsch. chem. Gesell 13, 1556.

[2] This Journal, 2, 130.

fact were made known to-day, for the first time, that the oxidation product obtained from mesitylenesulphamide is a monobasic acid, most chemists would, we think, consider it very probable that the product has the formula first provisionally assigned to it, according to which the sulphamine group is in the ortho-position with reference to the two methyl groups. This would appear all the more probable from the fact that when nitromesitylene and brommesitylene are oxidized, the nitro-group and the bromine atom actually protect the two ortho-methyls, as has been proved by Schmitz.[1] At the conclusion of his paper Schmitz says: "Das Brom und die Nitrogruppe üben also einen schützenden Einfluss auf die benachbarten beiden Methylatome aus."

We regret to say, however, that the conclusion which appears so probable has proved to be incorrect. In the first paper on this subject it was shown by a number of analyses that the product of oxidation under discussion is in reality one of the class of sulphinides; it is sulphaminemesitylenic acid less the elements of water. This suggested at once that possibly our first conclusion was wrong. Jacobsen's experiments,[2] which were taken up in the mean time, also indicated clearly that our first formula was not in accordance with all the facts.

To still further test the matter, which is one of considerable importance, we have started from mesitylenic acid and from this made the sulphonic acids. These were separated, and one of them converted, on the one hand, into ordinary oxymesitylenic acid, and, on the other, into mesitylenic sulphinide; thus proving that the sulphinide or the oxidation product in question has a structure analogous to that of ordinary oxymesitylenic acid. As Jacobsen had previously shown that his parasulphaminemesitylenic acid corresponds to a new oxymesitylenic acid, which is called paraoxymesitylenic acid, the proofs in regard to the nature of the sulphinide are complete.

Sulphomesitylenic Acids.

In preparing mesitylenic acid we followed at first the directions originally given, using nitric acid of sp. gr. 1.4, diluted with twice its volume of water. It was soon found, however, that the yield was very small, large quantities of nitromesitylenic acid being formed. According to our experiments a much larger yield is

[1] Annalen der Chemie, **193**, 160. [2] Ibid. **206**, 167.

obtained by using more dilute nitric acid, and we recommend the use of acid of sp. gr. 1.35, diluted with twice its volume of water. The mesitylenic acid was purified in the usual manner, and, when dry, subjected to the influence of the fumes of sulphuric anhydride for about forty-eight hours. At the end of this time the greater part of the acid had passed into solution, forming a dark viscous liquid. It was largely diluted with water and filtered from some unchanged acid, and was then of a beautiful red color. Neutralization was effected with chalk, and the filtered solution of the calcium salts decolorized with animal charcoal. The salts are easily soluble in water, and cannot be readily separated from each other. By repeated recrystallizations two salts were obtained in well-formed crystals, differing somewhat from each other, though by no means markedly. The less soluble salt is designated as the α-salt, and the other as the β-salt. Both were analyzed. The α-salt gave the following results:

I. 0.2011 gram salt lost 0.0411 gram H_2O, and gave 0.08378 gram $CaSO_4$.

II. 0.1757 gram salt lost 0.0358 gram H_2O, and gave 0.0735 gram $CaSO_4$.

Calculated for $C_6H_2\begin{cases} SO_3 \\ CO_2 \\ CH_3 \\ CH_3 \end{cases}$ Ca $+ 4H_2O$.		Found. I.	II.
Ca	14.93	15.40	15.45
$4H_2O$	21.18	20.44	20.38

The results with the β-salt were almost exactly the same as those just given.

I. 0.2586 gram lost 0.0529 gram H_2O and gave 0.1043 gram $CaSO_4$.

II. 0.2071 gram lost 0.042 gram H_2O and gave .0835 gram $CaSO_4$.

Calculated.		Found. I.	II.
Ca	14.93	14.87	14.91
$4H_2O$	21.18	20.28	20.45

The deficit in the water is probably to be referred to efflorescence, as the crystals lose their lustre to some extent on exposure to the air.

Whether we have actually to deal with two salts is perhaps a question, but it is not a question of much importance, as far as the use to which the salts are put in this investigation is concerned.

The main point to be attended to, a point of vital importance for our purpose, was to secure at least one salt of a sulphomesitylenic acid in unquestionably pure condition, and this we have done.

We attempted a separation of the two acids by preparing the barium salts, but our attempts were not attended with much success. One of the barium salts is exceedingly difficultly soluble. This was repeatedly boiled with water to extract any soluble salt that might be present, and then remained in the form of a heavy amorphous powder which, on analysis, was found to contain 37.3 per cent. barium, the calculated amount being 37.53 per cent. The soluble barium salt was not obtained in anything like pure condition and was not further examined.

Transformation of α-Sulphomesitylenic Acid into the Sulphinide.

The α-calcium salt above referred to was converted into the corresponding potassium salt and the solution evaporated to dryness. One-half of this potassium salt of α-sulphomesitylenic acid was treated with phosphorus pentachloride and ammonia. Most of the chloride formed in the first reaction dissolves in ammonia. On filtering from a small quantity of material, the nature of which was not determined, and adding hydrochloric acid, a copious precipitate was obtained. This proved to be nothing but mesitylenic sulphinide. Its appearance, fusing point, solubility and general conduct could not leave a doubt in regard to the identity of the two substances. The reaction suggests one described some time since by Remsen and Fahlberg[1] in connection with orthosulphobenzoic acid. This acid when treated with phosphorus pentachloride and ammonia is converted into benzoic sulphinide. Other similar cases have since been observed in this laboratory. In all of them the common feature of the compounds concerned is the ortho-position of the sulpho-group and carboxyl, so that it appears probable that in α-sulphomesitylenic acid also these two groups are in the ortho-position with reference to each other, and consequently that, in the sulphinide, a similar relation exists between the residues of sulphamide and carboxyl.

The formation of mesitylenic sulphinide by the reaction above described appears strange when we remember that the sulphinide itself when treated with the same reagents is converted into a new product fusing at 287°, probably a double amide.[2] On taking

[1] This Journal, **1**, 426. [2] This Journal, **2**, 143.

some of the sulphinide prepared by us, converting it into the potassium salt and treating it with phosphorus pentachloride and ammonia, a new substance was obtained identical with that obtained from the original sulphinide. The two substances were carefully compared with each other and no difference observed. Both fused at 288° according to our thermometer; both are very difficultly soluble in water, and both crystallize in very delicate needles. This supposed double amide is not decomposed by hydrochloric acid even when the latter is concentrated and boiling, so that it is plain that this is not the product first obtained from α-sulphomesitylenic acid, as might be supposed. The facts are probably these: When potassium sulphomesitylenate is treated with phosphorus pentachloride, only one of the acid hydroxyl groups is replaced by chlorine. On now treating this chloride with ammonia, the ammonium salt of sulphaminemesitylenic acid is formed, and the addition of hydrochloric acid precipitates the sulphinide. It is possible that the substance above referred to as insoluble in ammonia may have been the double chloride of sulphomesitylenic acid, and that this resists the action of ammonia. When the potassium salt prepared from the sulphinide is treated with phosphorus pentachloride, the chloride is easily formed, and this is readily acted upon by ammonia and converted into the diamide. As yet these statements lack proof.

Transformation of α-Sulphomesitylenic Acid into Ortho-oxymesitylenic Acid.

The second half of the potassium salt used in the last experiment was fused with potassium hydroxide, and the corresponding oxy-acid was readily obtained. The latter was precipitated on acidifying the alkaline aqueous solution of the fused mass. It was filtered off and washed and then brought into a flask with water and boiled. It passed over readily with the water vapor, and was thus easily obtained in pure condition. All the properties of the substance are those of ordinary oxymesitylenic acid. It fuses at 176°, and its solution is colored blue by ferric chloride. It is difficultly soluble in water. These properties, when taken together with its volatility with water vapor, prove that it is identical with ortho-oxymesitylenic acid. No trace of para-oxymesitylenic acid could be detected, though ether extracted a small quantity of a second

acid from the original mother liquor from oxymesitylenic acid. This was certainly not para-oxymesitylenic acid, but rather, in all probability, an oxyuvitic acid. Its quantity was too small to permit of its thorough examination.

Thus it will be seen that, while mesitylenic sulphinide, when fused with potassium hydroxide, is converted into mesitylenic acid, the corresponding sulphonic acid acts as such acids usually do, yielding the oxy-acid.

The most important result of this investigation is the conversion of a pure potassium salt of sulphomesitylenic acid into mesitylenic sulphinide on the one hand, and into ortho-oxymesitylenic on the other. The proofs of the structure of mesitylenic sulphinide are thus complete.

REVIEWS AND REPORTS.

Report on Progress in Physiological Chemistry.

Salivary Digestion and the Products formed.

In 1831 Leuchs made the interesting discovery that saliva, the first digestive fluid with which food comes in contact, possessed the property of converting insoluble starch into soluble dextrin and sugar. Later it was found that saliva exercised this property only slowly and with difficulty upon raw starch, while roasted starch and starch paste, in which the individual starch grains were ruptured, were rapidly converted into soluble saccharine products. This important property of saliva was soon ascribed to the presence of a peculiar diastatic ferment, which received the name of ptyalin, a small quantity of which was supposed to possess the property of converting an indefinite amount of starch into sugar without being itself used up or destroyed. According to Paschutin's[1] observations, however, the ferment of saliva can convert only a limited quantity of starch into dextrin and sugar, for saliva which has once served this purpose, on being used a second time works with much less activity than when fresh, and this appears to be independent of any hindering action due to the presence of the products of digestion.

The old and generally adopted view in regard to the decomposition of starch by salivary and similar ferments as well as by dilute sulphuric acid, was that the starch was first converted into isomeric

[1] Centralbl. f. d. med. Wiss. 1871, 24.

dextrin, and then further changed by taking up a molecule of water into dextrose. In 1860, however, Musculus,[1] while studying the action of diastase on starch, was led to the belief that the formation of sugar was the result of a splitting up of the starch molecule according to the following equation:

$$3C_6H_{10}O_5+2H_2O=C_6H_{12}O_6+2C_6H_{10}O_5,$$

inasmuch as he found that a mixture of diastase and starch heated at 70°C gave a fluid in which dextrose and dextrin were always present in the proportion of 1 : 2. Later, Payen,[2] and still later, Schulze and Märker,[3] have shown conclusively that diastase converts only a limited quantity of the starch into dextrose, and that no matter how great the excess of ferment or the length of time the action is continued, the quantity of sugar formed never exceeds 53 per cent. This amount of sugar agrees very closely with the quantity required on the supposition that two molecules of starch break up into equal molecules of dextrin and dextrose according to the following formula:

$$2C_6H_{10}O_5+H_2O=C_6H_{10}O_5+C_6H_{12}O_6.$$

That a dextrin is formed under these circumstances, which withstands the further action of diastase, has been recently and clearly shown by Musculus and Gruber,[4] who subjected starch paste to the action of diastase for five consecutive days, and then separated the remaining dextrin by precipitation with alcohol. The dextrin thus formed, on being tested, was found to be wholly unaffected by the further action of diastase. The exact expression of this decomposition is naturally dependent, in part at least, on the composition of the starch molecule, a fact which is not yet wholly settled. That the starch molecule is much larger than hitherto supposed is more than probable, and the researches of Bondonneau, Sachsse, and particularly Nägeli,[5] would seem to indicate that its composition is more correctly expressed by the formula $C_{36}H_{62}O_{31}$, which is exactly six times $C_6H_{10}O_5$+one molecule of water.

The next knowledge gained in regard to the decomposition of starch by ferments tended to complicate the question still further, for it was found that instead of there being only one dextrin, there were at least two, possessed of widely different qualities. At the same time Brücke[6] found that starch grains contain three distinct substances, granulose colored blue by iodine, erythrogranulose colored red, and cellulose, which either remains unchanged or is colored slightly yellow by iodine. Thus, when a small quantity of starch is mixed with a few drops of a strong iodine solution, the starch grains are colored deep blue, owing to the excessive amount of granulose, but if a small quantity of a dilute iodine solution is added to starch suspended in water and the mixture thoroughly shaken to ensure equable distribution of the iodine

[1] Chem. Centralbl. 1860, 603.
[2] Chem. Centralbl. 1865, 845.
[3] Chem. Centralbl. 1872, 823.
[4] Zeitschrift für Physiolog. Chem. 2, 177.
[5] Beiträge zur Kenntniss der Stärkegruppe, 34.
[6] Sitzungsber. d. Wiener Acad. III Abtheil. 1872.

among all of the starch grains, a pale red color is obtained. This reaction is due to the fact that the erythrogranulose, which is present in relatively smaller quantity in starch, has a stronger affinity for iodine than the granulose has, and consequently when but a small quantity of iodine is present the erythrogranulose combines with it exclusively, leaving the granulose and cellulose uncolored. Now, when starch is boiled with very dilute sulphuric acid, it is converted first into soluble starch or the amidulin of Nasse, and then into dextrin and sugar,[1] but in investigating the different stages of this change Brücke found two distinct kinds of dextrin. Thus, by the first action of boiling dilute sulphuric acid or of diastase, the granulose and then the erythrogranulose, are converted into a dextrin colored red by iodine, called erythrodextrin. By the further action of the dilute acid or of diastase this dextrin is changed into achroodextrin, which is not colored by iodine, and sugar. The achroodextrin by the combined action of acids or of ferments remains unchanged, or is but slowly decomposed, and this fact according to Brücke constitutes the main grounds of distinction between erythro- and achroodextrin.

That a certain quantity of saliva will act only on a certain quantity of starch is likewise made clear by the fact that the products of this transformation are variable, depending on the quantity of saliva employed; thus it has been found by experiment[2] that when a proportionately large quantity of saliva and a relatively small quantity of starch paste are employed, scarcely any erythrodextrin is found, this product being almost immediately further converted into achroodextrin and sugar. When on the other hand a very small quantity of saliva and a large quantity of starch paste are taken, considerable quantities of erythrodextrin are found. Thus these facts tend to corroborate Paschutin's observations that the ferment of saliva can convert only a limited quantity of starch into sugar, while at the same time it would appear that the first action of saliva consists in converting the granulose and erythrogranulose of starch into erythrodextrin, and this is followed, when sufficient ferment is present, by the further conversion of erythrodextrin into achroodextrin and sugar.

The ptyalin of saliva does not appear to differ from the diastatic ferment of the pancreas and other glands, and is likewise very similar in its action to extract of malt, excepting in the temperature at which the conversion of starch takes place. On the authority of Paschutin and Kühne, human saliva diluted ten times converts starch into dextrin and sugar most rapidly at 35–41° C, while the strongest action of malt ferment is at 70° C. In 1877 O. Nasse[3] attempted to show that the sugar formed from starch, glycogen, and likewise from Brücke's achroodextrin, by the action of saliva was not dextrose, but a saccharine body possessed of peculiar

[1] Discovered by C. Kirchhoff in 1811. [2] Brücke loc. cit.
[3] Pflügers Archiv. f. p. ges. Physiol. **14**, 473.

properties. This substance, which Nasse called ptyalose, possessed only half as great a reducing power as dextrose, was less soluble in alcohol, and was converted into dextrose by boiling with dilute sulphuric acid. In 1878 V. Mering and Musculus[1] called attention to the old statement of Dubrunfant, made in 1847, that by the action of malt on amylum a sugar was formed which was not dextrose, and which he termed maltose. This statement was for some time doubted, but recently the above investigators, calling attention to the works of O. Sullivan and E. Schultze,[2] have attempted to confirm this view. Maltose, $C_{12}H_{22}O_{11}+H_2O$, differs from dextrose by possessing a rotatory power three times greater and one-third as great a reducing power. By boiling with dilute acids, maltose is changed into dextrose, and it may thus be considered as a body intermediate between dextrin and dextrose. Now, the fact that starch, under the influence of diastase, is converted into maltose, and not into dextrose, has led Musculus and Mering to the supposition that starch, and likewise glycogen, under the influence of other ferments, as saliva and pancreas, may be converted into maltose, although not, perhaps, as an end product. They find, as a result of careful investigation,[3] that the action of saliva on starch is completely analogous to the action of diastase, viz. achroodextrin and maltose are formed, together with a small quantity of dextrose, the latter being present to the extent of 1 per cent, while the quantity of maltose is about 70 per cent. Nasse's[4] view that a new saccharine body ptyalose is formed is shown by Musculus and Mering to be incorrect. At the same time Nasse's statement that his ptyalose has its reducing power increased twofold by boiling with acids prepares us for the statement of Musculus that the so-called ptyalose is a mixture of maltose, dextrin and possibly a little dextrose. Glycogen prepared from liver treated with saliva for ten hours at 15°C yielded Musculus and Mering an achroodextrin which possessed the property of reducing alkaline copper solutions, maltose and small quantities of dextrose. The same result was obtained by the action of diastase. The same products were also formed by the action of pancreatic ferment on starch, in every case maltose being the predominant product.

Musculus, in conjunction with Gruber,[5] has likewise found that starch, by the action of diastase or acids, in splitting up with formation of maltose, soluble starch, dextrose and dextrin, gives rise to different kinds of achroodextrin, which are distinguished one from the other by the ease or difficulty with which they are attacked by ferments, as well as by certain differences in their chemical properties.

[1] Zeitschrift für Physiolog. Chem. 1, 395.
[2] Bericht. d. deutsch. chem. Gesell. 7, 1047. Schultze found that, by the action of vegetable diastase on amylum, achroodextrin and maltose were formed, the latter of which differed essentially from Nasse's ptyalose.
[3] Zeitschrift für Physiolog. Chem. 2, 403.
[4] Pflügers Archiv. 14.
[5] Zeitschrift für Physiolog. Chem. 2, 177.

Thus the following table represents, according to these investigators, the different products formed from starch by diastase:

	Rotatory Power.	Relative Power of Reduction.	Iodine Reaction.
Soluble Starch,	218°	6	red (blue.)
Erythrodextrin,	...	...	red.
α Achroodextrin,	210°	12	colorless.
β "	190°	12	"
γ "	150°	28	"
Maltose,	150°	66	"
Dextrose,	56°	100	"

Recently Dr. E. H. Bimmerman,[1] of Amsterdam, has confirmed the results of Musculus and Mering; for, by digesting 100 grams of potato starch with 1 litre of water and 800 cc. of filtered mixed saliva for five hours at 30–40°C, he obtained crystallized maltose, a dextrin possessing reducing properties, and a small quantity of dextrose. Bimmerman has likewise studied the changes which these products of salivary digestion undergo in the blood, and, as a result of his work, finds that when maltose is injected into the blood of a rabbit, for example, the urine contains maltose and dextrose, thus showing that maltose in the blood is partly changed into dextrose and partly excreted by the organism undecomposed. Soluble starch or amidulin injected into the blood in a similar manner was found to be wholly changed into dextrin and dextrose, both of which were detected in the urine. Achroodextrin α under the same circumstances was found to be only partially decomposed, the decomposition products being dextrose and maltose.

Carrying the experiments still farther, Bimmerman[2] finally arrives at the conclusion that starch in the blood undergoes changes in the same manner as by animal and vegetable diastatic ferments outside the body. Thus, for example, soluble starch and dextrin α readily yield under the influence of changes taking place in the blood. readily-fermentable sugar, dextrin β difficultly fermentable sugar, and dextrin γ none at all, which is in accord with the action of ferments outside of the body. Maltose, on the other hand, which is not attacked by ferments, undergoes, in contact with the circulating blood, a slight, but still appreciable, change into dextrose, while dextrin γ in the circulating blood yields no sugar, but is apparently converted into another form of dextrin, which possesses a higher reducing power, and to which the name dextrin δ has been given; a compound which also appears to be formed whenever amylum or starch is attacked very energetically by ferments or dilute acids. Seegen,[3] of Vienna, has also studied the action of salivary and pancreatic ferments on glycogen and other forms of amylaceous matter, and, he, too, has come to the conclusion independently of Musculus that the sugar formed from both glycogen

[1] Pflügers Archiv. **20**, 201. [2] Loc. cit. 209–210. [3] Pflügers Archiv. **19**, 122.

and starch by the action of saliva, pancreas, and diastase is not dextrose, but a sugar possessed of less reducing power and a higher specific rotatory power. Thus, by the action of saliva on glycogen, a sugar was formed having a specific rotatory power of 119°, which is more than twice as great as that of dextrose, and a reducing power amounting to 68 per cent., which is about one-third smaller than that of dextrose.

According to his observations also glycogen is, under the influence of ferments, quickly converted into achroodextrin. This change is finished when the original opalescence of the glycogen solution is changed to a clear and transparent one, but the achroodextrin according to Seegen is now further altered; it is partly converted into sugar, and at last when no further formation of sugar takes place a dextrin remains which has no reducing properties, is not further altered by ferments, which is insoluble only in very strong alcohol, and is converted into sugar by the action of acids, only when heated in sealed tubes. Thus on account of its very pronounced resistance to the action of ferments and acids Seegen has given it the name of *dystropodextrin.*

The ultimate conclusions which Seegen arrives at are, that at the end of the fermentation only 60 to 70 per cent. of the glycogen is converted into sugar by saliva or pancreas extract, and that the sugar formed is not dextrose, as it possesses a much smaller reducing power and a higher specific rotatory power. Diastase acts in a similar manner. By the same ferment starch is converted not into dextrose, but into a sugar possessing the same properties as that formed from glycogen, a sugar which he calls ferment sugar. When boiled with acids (HCl or H_2SO_4), even then only about 75 per cent. of the glycogen is converted into sugar, but in this case it appears to be dextrose which is formed. A *complete* change of glycogen into sugar takes place only when it is heated with acids in sealed tubes for 36–48 hours in a water-bath at 100°C.

The sugar formed from glycogen in the liver, however, appears to be dextrose, and inasmuch as the author was unable to extract any ferment from the liver, possessed of diastatic properties, other than a minimal action, he thinks it quite probable that the formation of sugar in the liver does not depend upon ferment action. It would now appear that while the results of Nasse and Seegen are in the main correct, and in reality substantiate the results of Musculus and Mering, their conclusions are vitiated by the manifest impurity of the so-called ptyalose and ferment sugar. Seegen's ferment sugar is, as pointed out by Musculus,[1] not a chemical individual, but is undoubtedly like Nasse's ptyalose, a mixture of maltose and dextrin with possibly a trace of dextrose. The properties assigned by Nasse and Seegen to their products are quite in accord with the results of Musculus and Mering; a combination of maltose with dextrin and a trace of dextrose would naturally give a higher specific rotatory power and less reducing power than dextrose.

[1]Zeitschrift f. Physiolog. Chem. **4**, 94, 1880.

The question has been raised recently in studying the action of ptyalin on glycogen, whether the glycogen obtained from the liver of an animal fed exclusively on carbohydrate food differs from the glycogen obtained from the liver of an animal fed on a purely albuminous diet. Schtscherbackoff[1] claimed to have demonstrated the existence of four distinct kinds of glycogen, for by boiling glycogen prepared from the liver of a dog fed on a mixed diet, with exceedingly dilute acids, he obtained four products characterized by specific rotatory power, reaction with iodine and with Fehling's solution. Seegen has likewise held it possible that liver glycogen may show a different resistance to those ferments which convert it into sugar, according as it has its origin from carbohydrates or albuminoids. But in 1877, Mering[2] attempted to show that these statements were incorrect and that only one glycogen is formed from different feedings, whether albuminous or carbohydrate, which reacts towards ferment, saliva, diastase, etc., in the same way. This idea is now substantiated by the fact that Musculus and Mering[3] have obtained from glycogen prepared by fibrin feeding and from amylaceous feeding, the same decomposition products.

According to the view generally accepted, human parotid saliva reacts more strongly alkaline than the saliva of other glands, but Astaschewsky,[4] who has lately investigated the question, has arrived at different results. He collected saliva from 16 different persons by means of fine glass tubes inserted into the ducts, and caused a flow of the secretion either by irritating the mucous membrane with ether vapor or by the mechanical act of chewing. The fresh saliva appeared thin fluid and showed no action whatever on turmeric paper, but on litmus gave an amphichromatic reaction. The more intensely the mucous membrane of the mouth is irritated the weaker becomes the acid reaction and the more rapidly appears the alkaline reaction upon violet or reddened litmus. The maximum of the diastatic action of parotid saliva corresponds with the strongest acid action. If the saliva is allowed to stand exposed to the air in open dishes, even in the cold, it becomes after a short time more or less turbid and no longer colors litmus red. Thus it appears that the fresh parotid saliva owes its acidity to the presence of carbonic acid or acid carbonates. It is further probable that the parotid saliva takes on its acid reaction first in the salivary tubes, as by very rapid secretion this reaction disappears, only to reappear again, however, after a short time.

Rapidity of Conversion of Starch into Sugar.—L. Solera[5] has attempted to answer the question how rapidly and in what quantities does human mixed saliva convert starch into sugar. By means of Fehling's solution he finds that at a temperature of 10–12°C the first traces of sugar appear in 12 seconds. On the other hand, he finds it takes a comparatively long time to convert the last residue of

[1] Ber. d. deutsch. chem. Gesell. **3**, 200. [2] Pflügers Archiv. **14**.
[3] Zeitschrift für Physiolog. Chem. **2**, 418. [4] Centralblatt f. d. med. Wissensch, 1878, **15**.
[5] Jahresbericht u. d. Fortschritte d. Thierchemie, 1879, 235.

the starch into sugar, for even after 20 hours a trace of unaltered starch can still be detected in the mixture, which; however, after 24 hours wholly disappears. If the mixture is composed of equal parts by weight of saliva and starch, or two parts of saliva to one of starch, suitably diluted with water, the starch entirely disappears in 14 hours.

On raising the temperature the rapidity of conversion is increased, thus at 35–40°C the last trace of starch entirely disappeared in 2½ hours from a mixture composed of equal parts of starch and saliva. A higher temperature (70°C) gives no increase.

Solera has also studied the behavior of different varieties of starch to saliva, viz. wheat, maize, rice and potato starch, and he finds that equal parts by weight of these different varieties of starch are not changed into equal parts by weight of sugar, and also that the conversion of the starch into sugar follows much more rapidly with certain kinds than with others; thus maize starch unites with proportionately the greatest rapidity of conversion the greatest absolute sugar production. Wheat and rice starch give ultimately equal quantities of sugar, although in different times, the wheat starch undergoes the change most rapidly, while potato starch which is changed quite rapidly into sugar yields the smallest absolute quantity.

Action of Saliva in the Stomach.—Various results have been obtained by different experimenters in studying the action of saliva in the stomach. This is naturally a very important question, since the mixture of amylaceous food and saliva is almost immediately carried into the acid gastric juice, where a possibly antagonistic ferment is active in a distinctly acid medium. A slight alteration of the reaction of saliva does not appear to destroy its diastatic action; thus, according to the experiments of Paschutin and Lehmann, as well as of others, the addition of very small quantities of alkali and acids have no influence on the alteration of starch by saliva, while, according to W. H. Watson,[1] the addition of very minute quantities of hydrochloric acid appears to increase the diastatic action. In solutions containing .2 per cent. of hydrochloric acid the diastatic action of saliva wholly ceases. Reinhard v. d. Velden[2] has, however, recently studied the character of gastric juice, taken by means of a pump from healthy human stomachs in different stages of digestion. He finds that, in the first stage of digestion, when the gastric juice is already strongly acid, free hydrochloric acid cannot be detected by fuchsine, methyaniline violet, etc. The time at which the hydrochloric acid can first be detected varies in different individuals, and appears in mixed diet to be dependent upon the quantity of food taken. Thus, after breakfast consisting of tea, bread and meat, the hydrochloric acid did not appear until ¾—1 hour, while after a complete dinner not until 2 hours. In gastric juice taken from the stomach soon, but not too soon, after

[1] Jour. Chem. Soc. 1879, 539.

[2] Zeitschrift für physiolog. Chem. 3, 205.

meal time, a solution of iodine in potassium iodide always gave a wine yellow color. Reinhard v. d. Velden also found that if starch paste and fresh human saliva were added to gastric juice in which the acidity was not due to hydrochloric acid, iodine gave only a bright yellow color. If, on the other hand, gastric juice containing hydrochloric acid was taken, iodine always showed a blue color, even when a large quantity of saliva was added and the test allowed to stand for a long time at 40° C. Thus it would appear that in the stomach there are two stages of digestion, separable one from the other—a first, in which the action of saliva can go on without hindrance, and a second, in which the pepsin alone is active; a stage of amylaceous and a stage of proteid digestion.

R. H. Chittenden.

Report on Analytical Chemistry.

[*Continued from p.* 71.]

Zinc.—*Separation from Cadmium.*—A. Yver.[1] The solution containing the two metals as acetates is treated with two or three grams of acetate of sodium and a few drops of acetic acid and then subjected to electrolysis. The battery used consists of two Daniell's cells of the usual form. The cadmium is completely precipitated upon the negative pole, while all of the zinc remains in solution. The deposition takes place in the cold and is complete within three or four hours, when the quantities of the metals range between 0.180 and 0.210 gram.

Separation from Copper.—G. Larsen.[2] A single precipitation with sulphide of hydrogen suffices for a complete separation of the two metals, provided the solution is acid with hydrochloric acid and hot when treated with the gas, and the precipitate is washed with a hot solution of sulphide of hydrogen containing hydrochloric acid.

Cadmium.—*Separation from Copper.*—G. Vortmann.[3] The dilute solution is treated with hyposulphite of sodium until it becomes colorless, and then heated to the boiling point. The copper precipitates as sulphide.

Silver.—*Electrolytic Deposition.*—H. Fresenius and F. Bergmann.[4] The tendency of silver to precipitate in a spongy or flocculent condition when deposited from an acid solution by electrolysis can be avoided by employing a weak current and dilute solution. The following conditions were found to be the most satisfactory: A solution containing in 200 cc. from 0.03 to 0.04 gram of silver and from 3 to 6 grams of nitric acid; a separation of the electrodes of one centimeter; a current sufficient to yield

[1] Bull. de la Soc. Chim. **34**, 18.
[2] Dingler's Jour. **239**, 239.
[3] Monatshefte für Chemie, **1**, 952.
[4] Zeitsch. f. analyt. Ch. 1880, 324.

from 100 to 150 cc. of electrolytic gas per hour. From a dilute neutral solution the silver deposits in a flocculent condition however weak the current.

Separation from Lead.—E. Donath.[1] The solution is treated with 4 or 5 cc. of glycerine, an excess of ammonia, and finally with 10 or 15 cc. of concentrated caustic potassa or soda. Complete solution ensues. The whole is then boiled four or five minutes, with constant stirring. Lead, also bismuth and copper, remains in solution, while the silver is completely precipitated as metal. The precipitate is washed with hot water, then with hot dilute acetic acid, and finally with hot water again. The washing with acetic acid is necessary in order to remove any carbonate of lead which may have formed in the filter during the first washing with water.

MERCURY.—*Detection in Dilute Solutions.*—J. Lefort.[2] It was shown by Orfila that the gold-tin voltaic couple of Smithson, devised for the detection of minute quantities of mercury, might lead to erroneous conclusions in consequence of the deposition of a portion of the tin upon the gold. It is, however, easy to distinguish a deposit of mercury from one of tin, since by placing the strip of gold foil in a narrow glass tube and heating, the former is readily sublimed, and its presence can be confirmed by exposing the sublimate to the vapors of iodine. A more curious difficulty presents itself when the solution to be examined contains arsenic. The couple reduces the compounds of arsenic quite readily with precipitation, first upon the tin and then upon the gold. When the latter is heated the arsenic sublimes, and cannot be easily distinguished in the sublimate from mercury, especially since the vapors of iodine convert it into a compound whose color resembles that of the iodide of mercury. This chance of mistaking arsenic for mercury should not be lost sight of when defective analyses are seemingly establishing the wide diffusion of mercury in mineral waters.

NICKEL AND COBALT.—H. Fresenius and F. Bergmann[3] have undertaken to ascertain the conditions most favorable for the electrolytic deposition of nickel and cobalt. They recommend for both a solution containing in 200 cc. from 0.1 to 0.15 gram of the metal as sulphate, from 2.5 to 4.0 grams of ammonia (NH_3), and from 6 to 9 grams of sulphate of ammonium; a current equivalent to 300 cc. of electrolytic gas per hour, and a separation of $\frac{1}{3}$ or $\frac{1}{2}$ cm. for the electrodes. If less ammonia is used the results are not good. Larger quantities retard the deposition, but do no further harm.

Qualitative Separation of Nickel and Cobalt.—F. Reichel.[5] Both metals are precipitated by caustic potassa. The precipitate, filtered but not washed, is placed in a test tube. A piece of solid

[1] Monatshefte für Chemie, 1, 789.
[2] Compt. Rend. **90**, 141.
[3] Zeitsch. an. Ch. 1880, 314.
[4] Zeitsch. an. Ch. 1880, 468.

potassium hydroxide and just enough water to dissolve it are added. On boiling the cobalt dissolves, and imparts a blue color to the solution. In this way minute quantities of cobalt can be expeditiously detected.

IRON.—*Precipitation by Succinate of Ammonium.*[1]—The statement of Fresenius that the precipitate of iron by succinate of ammonium is partially redissolved by heating has been found to be incorrect. The filtrate contains less iron than when the precipitation has been effected in the cold. Hot succinic acid dissolves very little of the precipitate, whether the precipitation has been effected in hot or cold solutions, but more in the latter than in the former case. Cold succinic acid dissolves more than hot. It is therefore recommended to precipitate from hot solutions and to boil two or three minutes before filtering.

ALUMINUM.—*Separation from Iron.*—E. Donath.[2] The neutral or slightly acid solution is treated with hyposulphite of sodium until all ferric compounds have been reduced. A solution of cyanide of potassium having twice the volume of the iron-aluminum solution, and containing from 15 to 20 grams of cyanide of potassium, is heated to boiling, and the iron-aluminum solution slowly poured into it. The solution is then quickly cooled, acidified with acetic acid, and the aluminum precipitated with carbonate of ammonium. If the aluminum hydroxide has not a pure white color, it must be dissolved and reprecipitated. The separation is quantitative.

MANGANESE.—*Use of Permanganate in Presence of Hydrochloric Acid.*—C. Zimmermann.[3] The usefulness of permanganate of potassium in volumetric analysis is considerably diminished by the fact that it cannot be used in solutions containing hydrochloric acid. The author has discovered that, by adding manganous sulphate, this difficulty can be wholly obviated. The solution in which the titration is to be made must, however, contain no free sulphuric acid.

Quantitative Determinations by Potassium Permanganate in Alkaline Solution.—E. Donath.[4] Hitherto this compound has been employed only in neutral or acid solution. Preliminary experiments, however, indicate that it can be successfully used in alkaline solution for the determination of both chromium and manganese. The reactions supposed to take place are as follows:

$$Mn_2O_7 + Cr_2O_3 = 2CrO_3 + MnO_2$$
$$3MnO + Mn_2O_7 = 5MnO_2$$

The standard solution of permanganate is rendered alkaline by addition of sodium carbonate and caustic soda, and heated nearly to boiling. The neutral solution of the chromous or manganous compound is then allowed to flow in until complete reduction of the permanganate has been effected.

H. N. MORSE.

[1] Jour. Chem. Soc. 1880, 674.
[2] Monatshefte für Chemie, **1**, 785.
[3] Berichte d. deutsch. chem. Gesellsch. 1881, 779.
[4] Berichte d. deutsch. ch. Gesellsch. 1881, 982.

NOTES.

Note to paper "Alkalimetry with Phenol Phthalein as Indicator."

A recent article on the subject mentioned in the title was prepared for this Journal before I had read Lux's paper on "Flavescin;"[1] otherwise I should have made the proper acknowledgment at that time of his priority in the general method of distinguishing alkalinity and causticity by an indicator which is indifferent to alkaline bicarbonates.

R. B. Warder.

Precipitation of Ammonium Phospho-molybdate in presence of Salts of Organic Acids.

In Fresenius' standard treatise on quantitative analysis appears the sentence: "Weinsäure und ähnliche organische substanzen verhindern die Fällung des phosphorsäuren Molybdänsäure Ammons ganz und gar (Eggertz)." This statement is certainly too strongly worded.

In a recent experiment one portion of the solution obtained by exhausting a "super-phosphate" with water and then digesting with solution of ammonium citrate (sp. g. = 1.09) was evaporated to dryness, the residue very carefully burned, redissolved with the aid of a little nitric acid, and ammonium molybdate with nitric acid in excess added as usual. A second portion of the same solution was treated directly with a large excess of strong nitric acid, and the ammonium molybdate added at once. There was no escape of gas or other sign of violent action on the citrate, which had been used to the full extent recommended by Fresenius, Neubaum and Luck.

The first portion gave 2.69 per cent.
The second portion gave 2.56 per cent.

of P_2O_5 on the superphosphate taken.

Hence the presence of ammonium citrate in large quantity only caused a loss of 4.83 per cent. on the P_2O_5 actually present; enough, of course, to make it necessary to burn off the organic matter, but clearly contradicting the last words of the sentence quoted above.

J. W. Mallet.

[1] Zeitsch. anal. Chem. 19, 457.

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ON OSMYL-DITETRAMIN.

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My researches on the metals of the platinum group were interrupted many years since by the want of a laboratory in which the separation and collection of osmic hyperoxide, OsO_4, could be effected without serious danger to the air-passages and to the eyes. As I may not be able to take up the subject again, I will here give the results of my study of a peculiar compound of osmium, oxygen, and the elements of ammonia, of much interest from a theoretical point of view.

In 1844[1] Frémy described a yellow crystalline substance which he obtained by adding ammonic chloride to a solution of potassic osmate, and to which he gave the formula,

$$2NH_4Cl.OsO_2.(NH_2)_2,$$

representing its formation by the equation,

$$OsO_4K_2+4NH_4Cl=2NH_4Cl.OsO_2.(NH_2)_2+2KCl+2H_2O.$$

In examining this salt I found that it gave a crystalline compound with platinic chloride, and a further study showed that it yielded

[1] Annales de Chimie et de Physique, 3d Series, 12, 522.

by double decomposition with salts of silver a well-defined crystalline sulphate, nitrate and oxalate. I therefore[1] proposed for it the formula,

$$4NH_3.OsO_2.Cl_2.$$

According to this view the formation of the salt may be represented by the equation,

$$4NH_4Cl + OsO_4K_2 = 4NH_3.OsO_2.Cl_2 + 2KCl + 2H_2O.$$

The subject was taken up some time after by Claus,[2] who ascribed to the chloride the formula,

$$4NH_3.OsCl_2 + 2H_2O,$$

so that it would be the osmium analogue of well-known compounds of palladium, platinum, iridium and ruthenium. If this view be correct, the formation of the salt would be represented by the equation,

$$4NH_4Cl + OsO_4K_2 = 4NH_3.OsCl_2 + 2KCl + 2O + 2H_2O.$$

It will be seen that Claus's formula requires that free oxygen should be given off in the formation of the chloride. In repeated preparations I have never found this to be the case. On Claus's view the chloride contains two molecules of water of crystallization. According to all analogy this water should be given off at a temperature below that at which decomposition of the salt itself takes place. To determine this point I heated a portion for an hour to successive temperatures of 100°, 115°, 130°, 140° and 154° C. The total loss after the five hours was 0.59 per cent., the salt being in appearance slightly decomposed. A loss of one molecule of water only would correspond to 4.84 per cent. These facts appear to me to show that the formula which I proposed is correct. Frémy's view would scarcely be defended by any chemist at the present time.

I propose to call the complex $OsO_2.4NH_3$, which we may for the sake of convenience consider as an integral part of each salt in the series, osmyl-ditetramin, to distinguish it from osmio-ditetramin, $Os.4NH_3$, which remains to be discovered, and which would correspond to the palladium, platinum, ruthenium and iridium salts above referred to.

[1] American Journal of Science, 2d Series, **25**, 248. [2] N. Petersb. acad. Bull. **1**, 121 and **6**, 179.

Chloride of Osmyl-ditetramin. When concentrated solutions of sal-ammoniac and potassic osmate are mixed, an orange-yellow crystalline precipitate of the chloride of osmyl-ditetramin usually separates at once. The potassic osmate should be added in small excess, and the salt after precipitation washed with cold water and dried *in pleno* over sulphuric acid. It is slightly soluble in cold water; hot water readily dissolves but soon decomposes it, with evolution of free osmic hyperoxide, OsO_4, and precipitation of a black powder. Strong chlorhydric acid precipitates the chloride from its solutions as a crystalline yellow or orange-yellow powder. The salt may be dissolved in hot water containing a little chlorhydric acid, and gives a deep orange-yellow solution, from which it separates, on cooling, in small deep brown-yellow crystals. The chloride is completely decomposed by ignition, leaving pure metallic osmium as a grey porous mass. It is necessary, however, as Frémy has stated, to ignite in a current of hydrogen to avoid loss by the formation of osmic hyperoxide. The decomposition by heat is expressed by the equation,

$$OsO_2.4NH_3.Cl_2 = Os + 2NH_4Cl + 2H_2O + 2N,$$

and furnishes perhaps the most simple and convenient method of obtaining pure metallic osmium. To prevent oxidation completely the osmium should be heated to a high temperature, and allowed to become cold in a current of hydrogen, which must afterward be displaced by carbonic dioxide and finally by air. Finely divided osmium oxidizes easily in the air, giving off vapors of osmic hyperoxide. It also exhibits in a remarkable degree the property possessed by spongy platinum, of causing the combination of oxygen and hydrogen, but the osmium is oxidized at the same time. This fact lends some support to the chemical theory of the action of platinum under the same circumstances.

Of the chloride:

0.7850 gram gave 0.4158 gram osmium = 52.96 per cent.

0.9520 gram gave 0.5065 gram osmium = 53.20 per cent.

0.6102 gram gave 80 cc. of nitrogen (moist) at 5° C. and 754.37 mm. = 15.87 per cent.

0.8667 gram gave 0.6813 gram AgCl = 19.45 per cent. chlorine.

1.1565 gram gave 0.3546 gram water = 3.46 per cent. hydrogen.

These analyses agree fairly well with the formula,

$$OsO_2.4NH_3.Cl_2,$$

which requires:

		Calc'd.	Found.		Calc'd.	
Osmium	199	53.78	53.20	52.96	53.15	194
2 Chlorine	71	19.19	19.45		19.45	71
12 Hydrogen	12	3.24	3.46		3.29	12
4 Nitrogen	56	15.14	15.89		15.34	56
2 Oxygen	32	8.65	...		8.77	32
	370	100.00			100 00	365

The osmium was determined by careful ignition in a current of hydrogen and afterward of carbonic dioxide. To estimate the chlorine, the salt was ignited with sodic carbonate and the reduced osmium separated by filtration.

Nitrogen was determined by Simpson's method, and hydrogen by combustion with oxide of copper. In judging analyses of this and similar compounds, it must be borne in mind that the salt is difficult to purify by repeated crystallization, on account of the facility with which it is decomposed, and also that the atomic weight of osmium is very uncertain. As will be seen, the analyses agree much better with the formula if we adopt for osmium the atomic weight proposed by Mallet,[1] 194, but I have not considered myself justified in changing the value generally received. Seubert[2] has recently shown that the atomic weights of platinum and iridium are lower than was supposed, and has suggested that the same is true in the case of osmium.

A solution of the chloride of osmyl-ditetramin gives with one of potassic ferro-cyanide a fine violet color. The reaction is very delicate, and affords the best method yet discovered for the detection of minute quantities of osmic hyperoxide in the wet way. In applying this test, the metal must first be oxidized. This may be easily effected by heating the alloy or compound of whatsoever kind in a silver crucible with caustic potash and potassic nitrate and then distilling the fused mass with nitric acid. The distillate is to be rendered alkaline by a small quantity of caustic potash, and then reduced to potassic osmate, OsO_4K_2, by a drop or two of alcohol or of a solution of potassic nitrite. A solution of ammonic chloride, sulphate or nitrate, is then to be added, after which potassic ferro-cyanide gives a more or less well-defined violet color. In this manner it is possible to recognize quantities of osmium too

[1]American Journal of Science, 2d Series, 29, 55, 56.
[2]Wiedemann's Annalen, B. 207, 1-50.

small to be detected by the characteristic odor of the hyperoxide.

Chlorplatinate. This salt is best prepared by boiling the finely pulverized chloride with a solution of platinic chloride. It forms beautiful orange-yellow crystals, slightly soluble in cold water.

Of this salt:

0.4800 gram gave 0.2608 gram osmium and platinum = 54.33 per cent., and 0.1308 gram platinum = 27.25 per cent., giving 0.1300 gram osmium by difference = 27.08 per cent.

The formula $OsO_2.4NH_3.Cl_2+PtCl_4$ requires 27.38 per cent. platinum and 26.82 per cent. osmium. In the analysis of this compound, the weight of the two metals was first obtained by reduction with hydrogen. The osmium was then volatilized by roasting the mixture in a current of oxygen at a red heat.

Sulphate. The sulphate, like the other salts of the series, is best prepared by pouring a solution of potassic osmate, OsO_4K_2, into a concentrated cold solution of ammonic sulphate. Its formation may be represented by the equation,

$$2SO_4(NH_4)_2+OsO_4K_2=OsO_2.4NH_3.SO_4+SO_4K_2+2H_2O.$$

The sulphate forms beautiful small crystals which have a fine orange-yellow color. It dissolves rather freely in hot, but slightly in cold water.

Of this salt:

0.7580 gram gave 0.3597 gram osmium = 47.45 per cent.

1.7484 gram gave 0.9933 gram SO_4Ba = 23.40 per cent. SO_4.

1.2396 gram gave 0.3972 gram water = 3.56 per cent. hydrogen.

0.6490 gram gave 0.2055 gram water = 3.51 per cent.

1.2067 gram gave 138 cc. nitrogen (moist) at 6.5 and 765.80 mm. = 13.99 per cent.

The analyses lead to the formula,

$$OsO_2.4NH_3.SO_4+H_2O.$$

		Calc'd.	Found.		Calc'd.	
1 Osmium	199	47.93	47.45		47.55	194
4 SO_4	96	23.36	23.40		23.53	96
14 Hydrogen	14	3.41	3.51	3.56	3.43	14
4 Nitrogen	56	13.62	13.99		13.72	56
3 Oxygen	48	11.68			11.77	48
	413	100.00			100.00	408

Nitrate. The nitrate is most easily prepared by pouring a solution of potassic osmate into a cold saturated solution of ammonic nitrate. The salt separates after a time in granular orange-yellow crystals which are paler in color than those of the sulphate. It is the least stable of the salts which I have examined, the cold solution being soon decomposed with evolution of free osmic hyperoxide.

Oxalate. The oxalate is the most stable salt which I have obtained. It is readily prepared by the process given for the other salts, employing of course ammonic oxalate. The salt separates in beautiful yellow or orange-yellow crystals, which are but slightly soluble in cold water. In this salt:

1.0345 gram gave 0.5133 gram osmium = 49.62 per cent.

1.1553 gram burnt with CuO gave 0.3441 gram water = 3.30 per cent. hydrogen and 0.2713 gram CO_2 = 6.40 per cent. carbon.

1.2817 gram gave 0.3834 gram water = 3.32 per cent. hydrogen.

1.8541 gram gave 234 cc. of nitrogen (moist) at 12.5° C. and 761.74 mm. = 14.94 per cent.

These analyses correspond tolerably well with the formula,

$$OsO_2.4NH_3.C_2O_4.$$

		Calc'd.	Found.		Calc'd.	
Osmium	199	51.19	49.62		50.78	194
C_2O_4	88	22.86	23.47		23.04	88
Hydrogen	12	3.11	3.30	3.32	3.14	12
Nitrogen	56	14.54	14.94		14.67	56
Oxygen	32	8.30			8.37	32
	387	100.00			100.00	382

As in the cases of the chloride and sulphate, the analyses correspond better with the assumption that the atomic weight of osmium is 194.

Claus obtained a solution of the oxide or hydroxide of osmylditetramin by digesting a solution of the chloride with argentic oxide. Jacoby first converted the chloride into sulphate by digestion with argentic sulphate, and then decomposed the sulphate with baryta water. The solutions thus obtained are yellow, alkaline, and very easily decomposed.

When a solution of potassic osmate is poured into a cold strong solution of hydrochloride of narcotin, cinchonin or strychnine, a

white precipitate is formed in either case which dissolves readily in dilute chlorhydric acid. The solutions give precipitates with platinic and auric chlorides. It seems at least possible that new bases are formed in which the higher alkaloids replace the ammonia of osmyl-ditetramin.

When a solution of potassic osmate is mixed with one of chloride of luteocobalt, $Co_2(NH_3)_{12}Cl_6$, a buff-colored precipitate is formed, which on addition of dilute chlorhydric acid becomes orange-yellow and beautifully crystalline. The salt dissolves in cold water without decomposition, but the solution is decomposed on gentle heating. It gives beautiful crystalline salts with auric and platinic chlorides. In the orange-yellow salt:

0.5647 gram gave 0.2642 gram cobalt and osmium = 46.70 per cent.

0.2642 gram of the mixed metals lost 0.2085 gram osmium as OsO_4 = 36.92 per cent., and gave by difference 0.0557 gram cobalt = 9.78 per cent.

0.4529 gram gave 52.5 cc. nitrogen (moist) at 17° C. and 765.9 = 13.51 per cent.

The ratios are here $OsCo_2N_{12}$, but further analyses are necessary to determine the constitution of the salt. The chlorides of the other cobaltamines also react with potassic osmate. My experiments in this direction were suggested by the reflection that the salts of the cobaltamines in certain points closely resemble the salts of ammonium.

When potassic osmate is mixed with a solution of the chloride of palladio-ditetramin, $Pd(4NH_3)Cl_2$, an orange-yellow or sherry wine colored solution is formed. The addition of chlorhydric acid throws down a fine orange-yellow crystalline precipitate. A solution of this salt gives an orange-yellow precipitate with platinic chloride.

The experiments detailed appear to show that interesting results will be obtained by pursuing the subject in the direction which I have pointed out. The very numerous class of metal amines offers a wide field for study.

I have also made some observations on other osmium bases which may be mentioned in this connection.

When ammonia is added to a solution of potassic osmate, the liquid immediately takes a sherry-wine color. After addition of an excess of chlorhydric acid and subsequent neutralization with

ammonia, the solution gives crystalline precipitates with ammonic oxalate, auric and mercuric chlorides, etc., and therefore contains a metalamine of some kind. As the osmiamines corresponding to platin-diamin, $Pt(NH_3)_2$, and platin-ditetramin, $Pt(NH_3)_4$, have not yet been obtained, it is possible that the base obtained by the action of ammonia upon potassic osmate may represent the osmium analogue of one of these.

The views of Blomstrand as to the constitution of the metalamines have found much favor with chemists, and appear to involve less that is purely hypothetical than any others which have been proposed. Applying this theory to the present case, it will be seen that osmyl-ditetramin chloride may be written either as

$$O_2{=}Os.4NH_3.Cl_2 \qquad O_2{=}Os\begin{cases} NH_3.NH_3{-}Cl \\ NH_3.NH_3{-}Cl \end{cases}$$

or as

$$Os{=}Os.4NH_3.Cl_2 \qquad Os\begin{matrix} \diagup O{-}NH_3{-}NH_3{-}Cl \\ \diagdown O{-}NH_3{-}NH_3{-}Cl \end{matrix}$$

The first view requires us to consider the osmium as tetratomic, while according to the second formula it would be diatomic. If we consider the osmium as diatomic, the chloride ought to form addition products with iodine and bromine, as for instance,

$$Os\begin{matrix} \diagup I \\ \diagup O{-}NH_3{-}NH_3{-}Cl \\ \diagdown O{-}NH_3{-}NH_3{-}Cl \\ \diagdown I \end{matrix}$$

I have sought in vain to form such compounds, and therefore consider the first view as the more probable of the two.

Devillé and Debray[1] have shown that ruthenium forms a hyperoxide the formula of which is RuO_4, and which is therefore the analogue of the osmium compound. The close resemblance between the two metals suggests the possibility of forming a ruthenium series similar to that of osmium which I have described, but I have made no experiments to test this suggestion, which I throw out for what it may prove to be worth.

With respect to the nomenclature employed, I may here remark that upon Blomstrand's theory of the constitution of the metal amines, it is possible to distinguish different modes of combination of ammonia by names which are not too cumbrous for ordinary

[1] Comptes Rendus, **83**, 926.

use. Thus we have two series of platinamines which we may write respectively,

$$Pt\begin{cases} NH_3-NH_3- \\ NH_3-NH_3- \end{cases} \quad \text{and} \quad Pt\begin{cases} NH_3- \\ NH_3- \\ NH_3- \\ NH_3- \end{cases}$$

In the first platinum is diatomic; in the second tetratomic. If we call the second "platino-tetramin," the first might be termed "platino-ditetramin," and in this manner the difference of atomicity, the number of atoms and the modes of combination of the ammonia are clearly expressed.

The experimental part of the work here published was finished long since. I[1] have delayed its publication in the hope of rendering it more complete, and especially of generalizing the results in various ways, some of which I have indicated above. The work is now given to the public, not as being complete or exhaustive, but simply in the hope that it will be found to contain suggestions which may be of use to other chemists working in the same direction.

CAMBRIDGE, *April 15th*, 1881.

NOTE ON THE COMPOSITION OF THE CARBONACEOUS RESIDUE FROM THE SOLUTION OF STEEL IN THE DOUBLE CHLORIDE OF COPPER AND AMMONIUM.

BY ANDREW A. BLAIR,

Chemist in Charge. Laboratory of U. S. Geological Survey.

While in charge of the laboratory of the U. S. Iron and Steel Commission at Watertown Arsenal, Massachusetts, in 1877, I was led to investigate the composition of the carbonaceous matter liberated from steel by the action of the double chloride of copper and ammonium; and as the results I obtained were at variance with those previously reported by others, I propose to give a short

[1] The first notice of the true character of Frémy's osmium salt was published jointly by Dr. F. A. Genth and myself (Am. Jour. Sci. *loc. cit.*). Circumstances prevented Dr. Genth from taking any part in the investigation, and I must therefore be held exclusively responsible for all that I have published upon the subject.—W. G.

account of them. I had hoped to follow up the work and present it in a more complete form; but as there seems to be no immediate prospect of my being able to do so, and as the work has remained untouched for four years, I venture to present these results, in the hope that they may be of assistance to some one following the same line of research.

Schützenberger and Bourgeois[1] treated white iron with copper sulphate, dissolved the precipitated copper in ferric chloride, filtered, washed, dried at 100°, and analyzed the carbonaceous matter with the following results:

Carbon	64.00
Water	26.10
Silicious Ash	8.10
Undetermined matter	1.80
	100.00

corresponding nearly to the formula $C_{22}.3H_2O$.

I used a steel of the following composition:

Sulphur	0.002	per cent.
Phosphorus	0.005	"
Silicon	0.095	"
Manganese	0.122	"
Cobalt	0.000	"
Nickel	0.000	"
Copper	0.010	"
Carbon	1.455	"

Drillings of this steel were treated with a large excess of the double chloride of copper and ammonium, and when all the copper first precipitated was redissolved, the carbonaceous matter was filtered off, washed with the double chloride acidulated with hydrochloric acid and finally with water, until the filtrate gave no precipitate with a crystal of silver nitrate.

It was then dried at a low temperature, thoroughly mixed in a platinum crucible, and kept for use in a desiccator. For the determination of carbon and hydrogen I used a glass tube 15 inches long and ½ in. in diameter. In the forward part about ½ in. from the cork of the calcium chloride tube was a piece of silver foil about

[1] Comptes Rend. 1875.

2 inches long, rolled tightly and completely filling the diameter of the tube; next to this 4 inches of coarse oxide of copper with an asbestos plug at either end.

A roll of copper wire thoroughly oxidized, 3½ in. long and of about the same diameter as the inside of the tube, came to within an inch of the back end of the tube, leaving a 3 in. space in the centre. The back end of the tube was connected by a perforated cork and glass tube with an oxygen holder and an air holder, so that dry pure oxygen or air could be passed through the apparatus at pleasure. The tube was placed in a gas combustion furnace 13 inches long, one inch of the tube projecting at each end.

About 0.2 gram of carbonaceous matter was put into a small platinum boat, and the boat into a glass test tube, the open end of which was provided with a cork covered with tin foil, to prevent access of air. This tube was then placed in an air bath heated to about 100° C. and the carbonaceous matter thoroughly dried. It was then taken from the bath, cooled in a desiccator and weighed. The tube, cork and empty boat having been previously weighed, the difference gave the weight of carbonaceous matter. The glass combustion tube, with a calcium chloride tube in the forward end, was heated to redness in the furnace and slowly cooled in a current of oxygen. When cool the calcium chloride tube was replaced by a weighed U tube containing dried calcium chloride, and a weighed potash bulb and drying tube (the latter protected by an additional drying tube to prevent its absorbing moisture from the outside air) were attached; the rear end of the tube was opened, the roll of oxidized copper wire withdrawn, the platinum boat pushed forward into the tube until it nearly touched the asbestos plug, and the roll of oxidized copper wire and the cork replaced as quickly as possible.

The forward end of the tube containing the roll of silver foil and the coarse copper oxide was first heated to redness (a current of oxygen passing through all the time), then the roll of oxidized copper wire and finally the boat, the heat being maintained until the carbonaceous matter was burned. The current of oxygen was replaced by one of air and the apparatus slowly cooled. When cold the calcium chloride tube and the potash bulb and drying tube were again weighed, the increase of weight in the former giving the water and that in the latter the carbon dioxide from the carbonaceous matter. The boat was carefully withdrawn and re-

turned to the test tube (which during the combustion had been kept in the desiccator) and the whole weighed as before. The loss of weight of course gave the amount of the volatile portion of the carbonaceous matter, and the increase of weight over that of the empty boat and the tube the amount of ash.

I expected of course to find the water, carbon and ash sum up to nearly 100 per cent., and was much surprised to find a deficiency of about 10 per cent. in my first analysis. I therefore repeated the operation several times with practically the same result.

The water varied only about 1.5 per cent. or from 20.50 per cent. to 22.00 per cent., while the carbon gradually decreased as the temperature and length of time of drying increased. When the carbonaceous matter was dried for about two hours at 95° to 100° C. I obtained 70 per cent. carbon, dried for 144 hours at 100° C. I obtained 64 per cent. carbon. Fearing some error in method or manipulation I then tried pure loaf-sugar in exactly the same way, and found

Carbon . . .	42.30
Water . . .	57.51
	99.81

This result was so satisfactory that I concluded I must look elsewhere for a reason for the deficiency in the carbonaceous matter; and it occurred to me that as steel contained nitrogen, that element might be found in the carbonaceous residue.

Careful determinations gave me nitrogen 0.45 per cent. I then thought that perhaps the carbon, at the instant of its separation, might take up chlorine from the copper chloride, as it takes up iodine and bromine when these elements are used in the decomposition of steel. A portion of the carbonaceous residue burned with pure lime gave me chlorine 2.59 per cent.

The only element left was oxygen. I therefore prepared a quantity of oxide of copper and made a direct determination of oxygen, following Stromeyer's[1] method, in sugar, when I obtained oxygen 51.47 and 51.42, theory 51.46.

As the carbon varied so much in the carbonaceous matter, it was necessary that the samples should be identically the same for the

[1]Ann. der Chem. und Phar. **117**, 247.

determinations of carbon and oxygen. Three small test tubes and platinum boats were therefore prepared, with a little wire rack to hold them, and three portions of carbonaceous matter weighed out as before.

After drying for several hours the rack was transferred to a desiccator, the tubes weighed, and while one boat was in the combustion tube I made an oxygen determination in the second portion and a chlorine determination in the third.

Two analyses resulted as follows:

	No. 1, dried 48 hours at 100° C.	No. 2, dried 144 hours at 100° C.
Carbon . . .	64.54 per cent.	64.30 per cent.
Water . . .	21.03 " "	20.28 " "
Excess of O .	8.01 " "	8.86 " "
Chlorine . .	3.76 " "	3.76 " "
Nitrogen . .	0.45 " "	0.45 " "
Ash	2.53 " "	2.45 " "
	100.32	100.10

These results certainly differ very materially from those obtained by Schützenberger and Bourgeois; but as theirs were obtained by treating the iron with copper sulphate, I thought it worth while to examine the carbonaceous matter liberated by this reagent as well. I obtained,

	I.	II.
Carbon	67.34 per cent.	67.17 per cent.
Water	22.83 "	22.50 "
Ash	2.15 "	2.08 "
	92.32	91.75

Leaving out the chlorine, these left about the same deficiency that there was in the partial analyses of the carbonaceous matter liberated by the action of the double chloride of copper and ammonium on the steel.

Another portion of the carbonaceous matter liberated by the action of the double chloride of copper and ammonium was heated in a glass tube in a current of hydrogen. It lost 39.25 per cent. of its weight, of which only 12.54 per cent. was water. There was no appearance of oily or tarry matter, and the residue did not appear crystalline, and burned off readily in oxygen.

Heated in hydrogen, lost	39.25	per cent.
Residue contained carbon	57.84	"
" " ash	2.91	"
	100.00	

If the 20 or 22 per cent. of water found by combustion in oxygen existed as hydrate, one would naturally expect to find it given off by heating; and if the oxygen in excess of the amount necessary to form water were merely occluded, one would expect it to unite with the hydrogen, thus forming an additional amount of water. As neither of these things occurs, it seems reasonable to suppose that the elements carbon, hydrogen and oxygen are combined in some more intimate way than as a hydrate of carbon.

So much remains to be done, however, before the nature of this residue can be known that I do not even venture to give a probable formula for it, and can only hope that this may lead some one to enter a field that certainly, to me, looks very promising.

NEWPORT, R. I.

Contributions from the Chemical Laboratory of Harvard College.

XII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.[1]

PARABROMBENZYL COMPOUNDS.

BY C. LORING JACKSON AND WOODBURY LOWERY.

Parabrombenzylalcohol ($C_6H_4BrCH_2OH$).—This substance was most easily prepared by boiling parabrombenzylbromide with water, in a flask with a return-cooler, for two or three days, until it no longer attacked the eyes. The reaction ran as follows:

$$C_6H_4BrCH_2Br + H_2O = C_6H_4BrCH_2OH + HBr.$$

The presence of the hydrobromic acid was established by treating the acid aqueous filtrate with argentic oxide, when argentic bromide was formed, and the solution became neutral. This method is analogous to that employed by Grimaux[2] for converting

[1] From the Proceedings of the American Academy. Communicated by the Authors.
[2] Grimaux, Comptes Rend. **70**, 1363; Ann. Chem. Pharm. **155**, 338.

tollylenebromide into tollyleneglycol, except that Grimaux heated the haloid compound with water at 170° to 180°, while we obtained the alcohol by boiling in a flask with a reverse-cooler. The alcohol was also obtained in the ordinary way by heating parabrombenzylacetate with aqueous ammonia in a sealed tube to 160°. In whichever way prepared it was purified by crystallization from ligroin, and its composition established by the following combustion:

0.2298 gram of substance gave 0.3765 gram of CO_2 and 0.0789 gram of H_2O.

	Required for $C_7H_8Br.OH$.	Found.
Carbon	44.92	44.69
Hydrogen	3.74	3.84

Properties.—It forms long elastic transparent colorless flattened needles, with a brilliant pearly lustre and a disagreeable odor; its vapor does not attack the eyes. Melting-point, 77°. It burns with a luminous green-bordered flame, distils with steam although slowly, and is very slightly soluble in cold, more freely in boiling water, easily soluble in alcohol, ether, benzol, and carbonic disulphide.

Parabrombenzylcyanide ($C_6H_4BrCH_2CN$) was obtained by boiling parabrombenzylbromide with an alcoholic solution of potassic cyanide as long as potassic bromide was formed: on addition of water a yellow oil was precipitated, which deposited crystals after standing for some time, and finally solidified completely. The crystals were drained on filter-paper, and purified by crystallization from alcohol. Their composition was determined by the following volumetric nitrogen determination:

0.3565 gram substance gave 20 cc. nitrogen under a pressure of 742 mm. and a temperature of 9°.

	Required for C_7H_6BrCN.	Found.
Nitrogen	7.10	6.58

Properties.—The substance separates from the oil at first obtained, either in flat truncated octahedra with a marked basal cleavage belonging either to the tetragonal or orthorhombic system, and having a very strong resemblance to the crystals of ferrocyanide of potassium, or else in flat twins imitating in a very beautiful manner the architectural form of the quatrefoil. These crystals are yellowish white, but the substance is rendered colorless by crystallization from alcohol; it has a disagreeable odor, does not attack the eyes,

melts at 47°, burns with a luminous green bordered flame, and is insoluble in water, moderately soluble in cold, freely in hot alcohol, soluble in ether and glacial acetic acid, still more readily in carbonic disulphide and benzol; by boiling with alcoholic potassic hydrate or heating in a sealed tube with hydrochloric acid it is easily converted into parabromalphatoluic acid.

Parabromalphatoluic Acid ($C_6H_4BrCH_2COOH$).—This substance was most easily obtained by heating the cyanide with crude fuming hydrochloric acid to 100° in a sealed tube. On cooling, the liquid was found to be full of shining flattened needles of the acid, another portion of which had fused on the side of the tube; this method gave better results more neatly than the saponification with potassic hydrate; the acid was purified by recrystallization from boiling water, and its composition established by analyses of its silver and copper salts. (See below.)

Properties.—It crystallizes in white glistening flattened needles with but little odor, melts at 114°, sublimes above its melting-point in little plates, and burns with the usual luminous green-bordered flame. It is but slightly soluble in cold, freely in boiling water, and in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. Ammonic and sodic hydrates dissolve it at once, forming the corresponding salts; it seems to decompose carbonates, but very slowly and imperfectly: potassic dichromate and dilute sulphuric acid convert it with some difficulty into parabrombenzoic acid.

In 1869, Br. Radziszewski[1] obtained a substance which he called parabromalphatoluylic acid, by the action of bromine in the cold upon alphatoluylic acid; he does not describe it fully, but only says that it crystallizes in prisms melting at 76°, and gives baric and calcic salts crystallizing in warts, and easily soluble in water and alcohol; by oxidizing it with potassic dichromate and dilute sulphuric acid he obtained nothing but parabrombenzoic acid melting at 251°. In the same operation another acid was formed containing bromine, which melted at 99°, and was not further examined.

The discrepancy between our results and those of Radziszewski has been shown by Bedson[2] recently to be due to the formation of both the ortho and para compounds when alphatoluic acid is treated with bromine. By converting the product into its barium salt Bedson has succeeded in isolating both the para and the ortho-

[1] Radziszewski, Ber. d. ch. G. 2, 207.

[2] Journ. Lond. Chem. Soc. 1880, 1, 90.

bromalphatoluic acids, and finds that the former melts at 114°-115°, the latter at 103°-104°, in agreement with our results.

Ammonic parabromalphatoluate, obtained by dissolving the acid in ammonic hydrate, and driving off the excess of ammonia on the water-bath, crystallized in long curving groups of colorless needles very soluble in water.

Argentic parabromalphatoluate ($C_6H_4BrCH_2COOAg$) was precipitated by adding the ammonic salt to argentic nitrate, as a white curdy mass similar in appearance to chloride of silver; it was washed with cold water, and dried at 60°.

0.3106 gram of the salt dissolved in dilute nitric acid, and precipitated with hydrochloric acid, gave 0.1375 gram AgCl.

	Required for $C_7BrH_6CO_2Ag$.	Found.
Silver	33.57	33.33

It is almost insoluble in water, perhaps a little more soluble in hot than in cold, but could not be obtained crystallized; it is readily soluble in dilute nitric acid; blackens slightly by exposure to the light, and even at a temperature of 60°.

Cupric parabromalphatoluate, $Cu(C_6H_4BrCH_2COO)_2$, was precipitated as a flocculent bluish green solid, on mixing cupric sulphate with the ammonic salt.

0.3028 gram of the salt gave 0.05028 CuO.

	Required for $Cu(C_8H_6BrO_2)_2$.	Found.
Copper	12.90	13.24

It is insoluble in water, but soluble in dilute hydrochloric acid.

The *baric salt*, obtained by neutralizing a solution of the acid with baryta water and evaporating, formed white indistinctly crystalline crusts easily soluble in water.

The *calcic salt* obtained in a similar way, and also, although very slowly, from calcic carbonate and a solution of the acid, appeared in the form of white warts; which, under the microscope, were seen to be globular groups of sharp needles looking somewhat like a chestnut bur; it was easily soluble in water.

The behavior of a solution of ammonic parabromalphatoluate with solutions of the following salts was also observed:

Mercurous salts, a heavy flocculent white precipitate.

Mercuric salts, a slight white precipitate.

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Plumbic salts, a heavy white precipitate, somewhat soluble in boiling water, and separating from this solution in crystalline flocks.

Ferric salts, a pale yellow amorphous precipitate, while chromic, aluminic, manganous, cobaltous, nickelous, zincic, and magnesic salts produced no precipitate.

Parabrombenzylsulphocyanate ($C_6H_4BrCH_2SCN$) was made by boiling the bromide with alcoholic potassic sulphocyanate and purified by crystallization from alcohol at low temperatures.

0.2318 gram of substance gave 0.2447 gram of $BaSO_4$.

0.3804 gram of substance gave 0.3125 gram of AgBr.

	Calculated for $C_7H_6Br.SCN$.	Found.
Sulphur,	14.03	14.50
Bromine,	35.09	34.95

Properties.—White ribbons often 5 cm. long, made up of needles united laterally; it has a strong odor similar to that of benzylsulphocyanate; melts at 25°, and is soluble in alcohol.

Parabrombenzylamines. Parabrombenzylbromide acts on alcoholic ammonia in the cold, giving a mixture of the three amines, or their bromides, from which the pure compounds can be easily obtained by washing out the bromide of the primary amine with water, treating the residue with sodic hydrate, and separating the secondary from the tertiary by crystallization from alcohol.

The *primary amine*, set free from its bromide with sodic hydrate, is an oil, which can be distilled with steam, and is soluble in ether; it is rapidly converted into the carbonate by exposure to the air.

The *carbonate*, obtained by treating the free base with carbonic dioxide, consists of little white prisms arranged in radiating groups, which melt at 131°–133°, are soluble in water and alcohol, insoluble or nearly so in ether, benzol, and carbonic disulphide.

The *chloride*, made from the carbonate with hydrochloric acid, forms flattened needles melting with apparent decomposition at 260°, soluble in water and hot alcohol, but slightly soluble in cold alcohol, and essentially insoluble in ether, benzol, and carbonic disulphide.

The *chlorplatinate*, $(C_6H_4BrCH_2NH_3)_2PtCl_6$, made from the chloride, and purified by washing with water, gave the following result on analysis:

0.3020 gram of the salt gave 0.0755 gram of Pt.

	Calculated for $(C_7H_6BrNH_3)_2PtCl_6$.	Found.
Platinum	25.16	25.00

It crystallizes in orange-brown plates, apparently of the monoclinic system, grouped in forms like frost, and is but slightly soluble in cold water, more so in hot, and in alcohol.

The *secondary amine*, $(C_6H_4BrCH_2)_2NH$, is left on evaporating its alcoholic solution as an oil, which solidifies on stirring, and can be obtained crystallized. It melts at 50°, and is very freely soluble in alcohol and ether.

The *chloride* is obtained in glistening rhombic scales, often pennately twinned, by adding strong hydrochloric acid to an alcoholic solution of the base; it melts at 283°, and is nearly insoluble in cold, somewhat more soluble in hot water or alcohol, insoluble in ether.

The *chlorplatinate*, $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$, formed by adding chlorplatinic acid to an alcoholic solution of the free base, after being washed with alcohol and dried at 100°, gave the following result on analysis:

0.4716 gram of salt gave 0.0802 gram of Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Platinum	17.58	17.01

It is a yellow powder, nearly insoluble in alcohol and water.

The *tertiary amine*, $(C_6H_4BrCH_2)_3N$, was purified by recrystallization from ether, or from ligroin; in either case a matted mass of needles looking like cotton was obtained, but the melting-point differed according to the solvent used, the crystals from ligroin showing the constant melting-point 92°, those from common ether the constant melting-point 76°–78°. Two recrystallizations from ligroin were enough to raise the melting-point of the crystals from ether to 92°, while the same number from ether lowered it again to 76°–78°. The following analyses, however, prove that the substance dried *in vacuo* has the composition of the tertiary amine, whichever solvent was used in its purification.

I. 0.3800 gram of the crystals from ligroin, m. pt. 92°, gave 0.6680 gram CO_2 and 0.1200 gram H_2O.

II. 0.2515 gram of the crystals from ether gave 0.4430 gram CO_2 and 0.0890 gram H_2O.

0.2020 gram of the crystals from ether gave 0.2175 gram AgBr.

0.1888 gram gave 0.2022 gram. AgBr.

	Calculated for $(C_7H_6Br)_3N$.	Found. I. (Ligroin.)		II. (Ether.)	
Carbon	48.09	47.93		48.03	
Hydrogen	3.44	3.51		3.93	
Bromine	45.81		45.82		45.56

Properties.—Fine white needles matted together into a woolly mass or forming circular radiated groups, insoluble in water, very slightly soluble in alcohol hot or cold, not freely in warm ether, but easily in hot ligroin, from which it crystallizes on cooling. In the preparation from alcoholic ammonia and parabrombenzylbromide it sometimes appears in needles 12 cm. long.

No definite chloride could be obtained even by precipitating the platinum as sulphide from the chlorplatinate, and washing with alcohol, as this gave only a viscous varnish.

Triparabrombenzylamine chlorplatinate $[(C_6H_4BrCH_2)_3NH]_2PtCl_6$, made by adding chlorplatinic acid to an ethereal solution of the free base, and purified by washing with water, alcohol, ether and ligroin, gave the following result on analysis:

0.3254 gram of the salt gave 0.0432 gram of Pt.

	Calculated for $[(C_7H_6Br)_3NH]_2PtCl_6$.	Found.
Platinum	13.51	13.28

Corn-yellow indistinct crystals, insoluble or nearly so in all the common solvents.

XIII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

THE RELATIVE CHEMICAL ACTIVITY OF CERTAIN SUBSTITUTED BENZYL BROMIDES.

The following paper contains an account of some experiments undertaken to compare the ease with which bromine can be removed from the side-chains of the substituted benzylbromides described in the first paper of this series: in other words, an attempt to establish some relation between the structure of a molecule and its chemical activity. The differences in structure, which I have taken up, are of two sorts,—those depending on difference in the position of the same element, as in the three monobrombenzylbromides; and those depending on the presence of different but related elements in the same position, as in parachlor-, parabrom-, and paraiodbenzylbromide.

After a careful consideration of the reagents by which the side-chain bromine could be removed from these substances in a simple metathetical reaction, I decided that sodic acetate promised the best results, and, after many experiments, adopted a method, which consisted in treating equivalent amounts of the substituted benzylbromides, for the same length of time and under the same conditions, with an alcoholic solution of sodic acetate, and determining by volumetric analysis the amount of sodic bromide formed from each according to the following general reaction,—

$$C_6H_4XCH_2Br+NaC_2H_3O_2=C_6H_4XCH_2C_2H_3O_2+NaBr,$$

in which X stands for the halogen atom attached to the benzol ring. But even this reaction, although less full of sources of error than most of those available, is not so well adapted to work of this sort as I could wish; since the action takes place so rapidly that small differences in the time of two experiments produce comparatively large differences in their results. I have tried, therefore, to make the time occupied in starting and stopping the action as short as possible, and have reduced the duration of the addition of the sodic acetate solution, by which the reaction is started, to five seconds; but I have not been so successful in stopping the reaction promptly, as this was done by precipitating the organic matter with water, of which so large a quantity was needed that the average duration of the addition was fifteen seconds.

This method of stopping the reaction by means of water is not above criticism; for, although I consider of little or no weight the possible objection that the reaction may continue forming more sodic bromide after the addition of water, yet the presence of even a small amount of the substituted benzylbromide will cause a serious error in the determination of the sodic bromide,[1] and it is very hard to remove this completely by filtration; that it is possible, however, if sufficient care is used, appears from the following experiment.

A mixture of parabrombenzylbromide and parabrombenzylacetate was dissolved in a little alcohol, and, after precipitating with

[1] This point is illustrated by the following experiments: A little parabrombenzylbromide was dissolved in alcohol, and precipitated with water; 2.30 cc. of a standard solution of argentic nitrate were added, and the mixture allowed to stand fifteen minutes; on titrating for silver, it was found that 0.41 cc., corresponding to 0.0069 gram of $AgNO_3$, had been lost, while another similar sample which stood for one hour and twenty minutes lost 1.59 cc., corresponding to 0.026 gram of $AgNO_3$.

water and filtering, 4 cc. of a standard solution of argentic nitrate added, upon titrating the liquid 5.3 cc. of the standard solution of potassic sulphocyanate were found to be necessary, the theoretical quantity being 5.27 cc.

In selecting a solvent, it was necessary to find one which would dissolve all the substances entering into the reaction; since Berthelot and Pean de St. Gilles[1] have shown that, when two liquids which do not mix are used, the amount of action depends to a large extent on the size of the surface of contact; and therefore no constant results can be expected. I have confirmed these observations, while studying the action of water on the substituted benzylbromides, as will be described later in this paper. Under these circumstances, alcohol seemed to be the only solvent admissible; but its use introduced a new source of error, since it acts on the benzylbromides, forming the corresponding ethyl ethers and hydrobromic acid, as is shown by the following experiment.

Some parabrombenzylbromide was boiled with absolute alcohol for fifteen minutes. After removing the organic matter by precipitation with water and filtration, a precipitate was formed on the addition of argentic nitrate.

This defect was removed as completely as possible by taking pains that the benzylbromides should be in contact with the alcohol for the same length of time in each series of experiments. Then the results depended, in each case, on two reactions, viz.:

$$C_6H_4XCH_2Br + NaC_2H_3O_2 = C_6H_4XCH_2C_2H_3O_2 + NaBr$$
$$C_6H_4XCH_2Br + C_2H_5OH = C_6H_4XCH_2OC_2H_5 + HBr$$

but, as the time of each was the same in all the experiments of a series, the occurrence of the second did not materially affect the result, especially as the amount of substance entering into this second reaction was very small.

The adjustment of the amount of alcohol to be used was no easy matter, because sodic acetate and bromide are very sparingly soluble in absolute alcohol, and any considerable dilution interferes with the solubility of the benzylbromides; nor could the difficulty be removed by increasing to any great extent the amount of alcohol, as this would have increased the length of time necessary to stop the reaction.

[1] Ann. Chim. Phys. 3d ser. **66**, 46; **68**, 238.

More important than any of the sources of error yet mentioned is that proceeding from the differences in volatility of the benzylbromides with alcohol vapor, since this must alter the amount of substance capable of entering into the reaction in each case by the quantity of bromide volatilized with the alcohol in the upper part of the flask; and it is principally to this cause, which I could find no way of removing, that I am inclined to ascribe the considerable variations in my results.

This discussion of the defects in the process shows that no absolute agreement in the numbers obtained can be expected; but they agree nearly enough to establish certain interesting relations between the rates of decomposition of some of these compounds.

Comparison of the Three Monobrombenzylbromides.

One gram of each substance was weighed in a wide-mouthed flask, the cork of which was fitted with a return-condenser and a short wide tube closed with a cork for the addition of the reagents, 10 cc. of absolute alcohol were added, and the mixture heated for seven minutes in a boiling water-bath. After which, 25 cc. of a saturated solution of sodic acetate in 99 per cent. alcohol, at 60° to 70°, were introduced, and the flask heated for a definite time, varied in each series of experiments; care being taken that the water-bath boiled violently during the whole time, and that the three flasks to be compared were immersed to the same depth, and arranged symmetrically in the bath. The action was stopped by the addition of a large quantity of water, the flask being removed from the bath at the same time; and, after filtering out the organic matter, the quantity of sodic bromide formed by the reaction was determined by Volhard's[1] excellent method of titration with sulphocyanate.

The brombenzylbromides used were made in the way described in the first paper of this series, and purified with the utmost care.

The sodic acetate was prepared by drying the crystallized salt in an air-bath. It yielded on analysis the following result:

0.7720 gram of $NaC_2H_3O_2$ gave 0.6655 gram of Na_2SO_4.

	Calculated.	Found.
Sodium	28.05	27.93

The absolute alcohol did not turn anhydrous cupric sulphate blue, and neither it, nor the acidified solution of the sodic acetate, gave a precipitate with argentic nitrate.

[1] Ann. Chem. u. Pharm. **190**, 1.

The 25 cc. of the alcoholic solution of sodic acetate contained a little more than enough of the salt to decompose the one gram of brombenzylbromide used, since,—

10 cc. of this solution yielded on evaporation 0.136 gram of sodic acetate, and therefore,—

25 cc. contained	0.340 gram
Needed for 1 gram brombenzylbromide .	0.328 gram
Excess	0.012 gram

The 35 cc. of alcohol present were much more than sufficient to dissolve all the sodic bromide formed, as a rough determination showed that,—

35 cc. of absolute alcohol dissolve 0.627 gram NaBr.

1 gram brombenzylbromide yields 0.412 gram NaBr.

All the substances, therefore, were in solution throughout the experiment.

The accuracy of the method was tested by the following experiments, in each of which two portions of parabrombenzylbromide were compared:

I. Time, five minutes.

A. 1 gram parabrombenzylbromide lost 0.1164 gram Br.
B. " " " 0.1102 gram Br.

Difference . . . . 0.0062 gram Br.

	Percentage of total side-chain bromine removed.	B in per cent. of A.
A.	36.39	100.0
B.	34.47	94.7
	1.92	5.3

II. Time, seven minutes.

A. 1 gram parabrombenzylbromide lost 0.1484 gram Br.
B. " " " 0.1446 gram Br.

Difference . . . . 0.0038 gram Br.

	Percentage of total side-chain bromine removed.	B in per cent. of A.
A.	46.36	100.
B.	45.21	97.5
	1.15	2.5

From these results it appears that the method can be trusted within 0.0062 gram of bromine, or 5.3 per cent. when the largest number is taken as 100.[1]

The results of the experiments, comparing the rate of decomposition of the three monobrombenzylbromides, are given in the following table; the first column of which gives the time from the addition of the acetate till the reaction was stopped by dilution with water, while in the other columns, under the name of each substance the amount of bromine removed is given,—first in grams, and second in percentages of the total amount of side-chain bromine.

TABLE I.

Time in minutes.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.
5	0.0855	26.73	0.0621	19.41	0.0533	16.65
10	0.1261	39.41	0.0968	30.25	0.0700	21.88
20	0.1752	54.75	0.1329	41.54	0.1015	31.72
30	0.1880	58.76	0.1517	47.43	0.1412	44 13

On representing the percentages of the total side-chain bromine removed by curves, in which horizontal distance represents time, vertical per cents, it is found that those given by the para and meta compounds are comparatively regular, but that the ortho curve is decidedly irregular. The same fact is brought out by the following table, in which the amount of bromine removed from the ortho and meta compounds in each experiment is given in percentages of the amount derived from the para compound in the same experiment.

TABLE II.

Time in minutes.	Para.	Meta.	Ortho.
5	100	73.	62.
10	100	77.	55.
20	100	76.	58.
30	100	81.	75.

[1]The results of these experiments cannot be compared with those given in Table I., because the quantity of alcohol used was not the same.

The differences between the relative amounts of bromine removed from the meta compound in the first three experiments, tabulated above, fall within the limit of error of the process, which amounts to over five per cent. when the numbers are given in this form; and, although the amount of bromine removed during thirty minutes is somewhat larger, the difference between this and the highest of the other numbers is only four per cent. It is probable, therefore, that the relative rate of decomposition for the para and meta compounds remains constant in the interval of time between five and thirty minutes; and that the slight increase in the numbers with the time in the experiments at 5, 20, and 30 minutes, is entirely accidental, although this point can be settled only by a new series of observations with a more accurate method. If this is assumed to be true, the mean of the numbers given in the meta column will represent the rate at which the metabrombenzylbromide is attacked, in comparison with that for the para compound taken as 100. This mean is 77; that is, about three-quarters as much bromine is removed from the meta as from the para compound in the same length of time.

The numbers given in the ortho column show much more serious deviations, the maximum difference amounting to twenty per cent.; but, as I observed that these numbers increased essentially with the time during which the specimen had stood exposed to the air of a desiccator, the experiments having been tried in the following order,—10 minutes, 55 per cent.; 5 minutes, 64 per cent.; 20 minutes, 58 per cent.; 30 minutes, 75 per cent.—I was led to the conclusion that the substance was undergoing decomposition, which afterwards was proved to be the case by the following analyses: I. made before, II. and III. after, the series of experiments.

I. 0.2375 gram of orthobrombenzylbromide gave, by the method of Carius, 0.3565 gram AgBr.

II. 0.2950 gram of substance gave 0.3705 gram AgBr.

III. 0.4100 gram of substance gave 0.5210 gram AgBr.

	Calculated for $C_7H_6Br_2$.	Found. I.	II.	III.
Bromine	64.00	63.87	53.46	54.07[1]

The complete study of this decomposition must be postponed till a future paper. I can only say here, that no appreciable amount

[1] As these experiments were made before the orthobrombenzylbromide was obtained in the solid state, I had no criterion of its purity except the analysis.

of free hydrobromic acid could be detected in the substance analyzed above, and that I have often found crystals of orthobrombenzoic acid in specimens of orthobrombenzylbromide which had stood exposed to dry air for several months. Whatever may be the nature of the change, it is evident that the ortho numbers are of no value; and no attempt was made to correct them by new experiments, because such an unstable substance as the orthobrombenzylbromide is entirely unfit for work of this sort.

I will add a number of other comparisons, which were made by less accurate processes during the elaboration of the method. They are given as in Table II., the amount of bromine removed from the para compound being taken as 100 in each experiment, and the amounts from the meta and ortho compounds given in percentages of this. Either two or four grams of substance were taken in each experiment.

TABLE III.

Time in Minutes.	Para.	Meta.	Ortho.
22	100	78	54
22	100	73	52
23	100	78	54
21	100	—	48
Mean,	100	76	52

These numbers, entitled to very little consideration as independent experiments, confirm the preceding results from the meta compound, even more closely than could be expected when the large limit of error is remembered: and further, would seem to indicate that the rate for the ortho compound is about one-half that for the para, if it is assumed, as before, that the relative rate does not vary with the length of time during which the reaction has run; a result confirmed by the experiment made first in the preceding series, and therefore entitled to the most weight, which gave 55 per cent.

Berthelot and Pean de St. Gilles,[1] in their classic researches on etherification, found that after a certain time the water set free in the reaction prevented further formation of the ether; in other words, that there was a limit to etherification. Although it did not seem probable that there would be such a limit to this reaction,

[1] Ann. Chim. Phys. 3d ser. 68, 225.

some experiments were tried to test the question, with the following results :—

I. Time somewhat more than two hours:

1 gram of parabrombenzylbromide lost 0.3203 gram of bromine.

1 gram of metabrombenzylbromide lost 0.2701 gram of bromine.

0.8200 gram of parachlorbenzylbromide lost 0.3082 gram of bromine.

To this may be added the following, in which the method was somewhat different; in II. common alcohol being used, and in III. the reaction taking place in a sealed tube, with dilute alcohol as the solvent.

II. Two portions of parabrombenzylbromide, 1 gram each, lost in twenty-five minutes 0.3113 gram and 0.3074 gram of bromine.

III. In thirty minutes 0.3046 gram and 0.3093 gram of bromine.

The results of these three experiments, calculated into percentages of the side-chain bromine, are given for the sake of comparison in the following table:

TABLE IV.

I.		II.		III.	
Para.	100.1	Para.	97.3	Para.	95.3
Meta.	84.4	"	96.1	"	96.7
Chlor.	96.4				

Owing to the different conditions under which they were made these series of experiments are not comparable with each other, or with the series given in Tables I. and II., even I. not having been made under exactly the same conditions; they show, however, that there is no limit to the reaction in the case of the parabrombenzylbromide and probably none in the case of any of these substances.

Action of Water on the Monobrombenzylbromides.

Another entirely different method was also tried, which consisted in heating the substituted benzylbromides with water in sealed tubes, and determining the amount of hydrobromic acid formed by the reaction,—

$$C_6H_4BrCH_2Br + H_2O = C_6H_4BrCH_2OH + HBr.$$

For this purpose one gram of each substance was weighed in a tube about 14 cm. long and 2 cm. wide; 5 cc. of water were

added, and, after sealing, the tubes were put into a hot chloride of calcium bath, provided with an air-tight tin cover carrying a return-cooler, which thus was kept at a constant temperature throughout the process. After a definite time the tubes were removed, cooled as rapidly as possible with cold water, and the contents washed into a beaker, and titrated with a standard solution of baric hydrate. The following experiments were made with two portions of parabrombenzylbromide to test the process.

	Time in Hours.	Temperature.	Percentage of side-chain bromine removed. Portion *a*.	Portion *b*.
I.	2	132°–134°	16.05	13.3
II.	$2\frac{1}{2}$	110°–134°	17.8	16.3

	I.	II.
a	100	100
b	83	92

The marked want of agreement between these numbers is undoubtedly due to the fact that the mixture was not homogeneous, and therefore the differences in size of the surface of contact between the water and benzylbromide in the different tubes had a marked effect on the result.

In spite of the inaccuracy of the method, two experiments were carried through with the following results:

TABLE V.

TEMPERATURE 135°.

Time in hours.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.
6	0.1421	43.85			0.0763	23.55
6	0.1268	39.15	0.0969	29.9	0.0918	28.35

These results calculated into the form of Table II. become:

Para.	Meta.	Ortho.
100		54
100	76	72

The very high number for the ortho compound in the second experiment is probably due to a previous decomposition of the substance similar to that observed in the principal series of experi-

ments. The other results, as far as they go, confirm those obtained by the acetate method.

In the following table all the numbers thus far obtained are compared:

TABLE VI.

ACETATE METHOD.

Time.	Para.	Meta.	Ortho.
5′	100	72	64
10′	100	77	55
20′	100	76	58
30′	100	81	75
21′	100	—	48
22′	100	78	54
22′	100	73	52
23′	100	78	54
WATER METHOD.			
6 hours	100		54
6 hours	100	76	72
Mean	100	76	59

A series of comparative experiments with parachlorbenzylbromide, parabrombenzylbromide and paraiodbenzylbromide was also made by the sodic acetate method, which indicated that they lose bromine at the same rate, when they are used in molecular proportions. I will give here, however, only the results from the last series of experiments, as in the others I did not succeed in overcoming some of the sources of error mentioned in the introduction wholly to my satisfaction. These results are given as in Table II.

Time in Minutes.	Parachlorbenzylbromide.	Parabrombenzylbromide.	Paraiodbenzylbromide
25	100	97	99

Summary.

The results of this investigation are,—1. The side-chain bromine is removed from the three monobrombenzylbromides approximately at the following rates:

	Para.	Meta.	Ortho.
	100	76	55 (?)
or	4	3	2 (?)

when the quantity removed is less than 60 per cent. of the whole.

2. From parachlor-, parabrom-, and paraiodbenzylbromide at essentially the same rate, if quantities proportional to their molecular weights are used.

All these results need confirmation by more accurate experiments, but, as Menschutkin in one of the papers[1] of his beautiful series on the rate of etherification (the first[2] of which was published a year after the appearance of a preliminary notice[3] of my work) has announced his intention of studying the effect of aromatic isomerism, and with his better chosen reaction and more delicate method will be able to do the work much more easily and accurately than I could, I have decided not to pursue the subject farther.

So far as I have been able to find, the only paper on this subject, as yet published, is one by Post and Mehrtens,[4] who describe a single attempt to make out the relative acidity of the three nitrophenols by treating weighed amounts of baric carbonate with solutions of the corresponding quantity of the three isomeres, and after one week determining the amount of baric carbonate dissolved. In this way they got results which calculated in percentages of the amount from the para compound become:

Para. m. pt. 115°.	Meta. m. pt. 96°.	Ortho. m. pt. 45°.
100	57	93

and, therefore, agree with mine neither in order nor ratio.

AN ABSTRACT OF THE RESULTS OBTAINED IN A RECALCULATION OF THE ATOMIC WEIGHTS.

By F. W. Clarke.

During the past three years I have been engaged upon a recalculation of all the atomic weight determinations which have been published from the time of Berzelius' earlier investigations down to the present date. My purpose has been to reduce all similar series of experiments to common standards; to calculate the probable error of each series; to combine the results into general means; and then to deduce the atomic weights in such a way that each

[1] Ann. Chem. Pharm. **197**, 225.
[2] Ber. d. ch. G. **10**, 1728.
[3] Ber. d. ch. G. **9**, 931.
[4] Ber. d. ch. G. **8**, 1549.

value should represent a fair average of all the trustworthy estimations. In other words, I have sought to bring together all the vast number of scattered details, and to derive from them a more consistent table of atomic weights than has hitherto been found in chemical literature. My complete work will appear in due time as a separate volume; my present intention is to give merely a summary of my methods, and my conclusions.

Taking hydrogen as unity, I necessarily began with the ratio between it and oxygen. This ratio has been determined accurately in only two ways: First, by the synthesis of water over copper oxide, and secondly, from the relative density of the two gases. Ignoring earlier inexact experiments, we may consider only the data furnished by Dumas, by Erdmann and Marchand, and by Regnault. From Dumas' nineteen syntheses of water, we get for oxygen values varying from O=15.892 to O=16.024. The mean of all is 15.9607, with a probable error of ± .007. Erdmann and Marchand give eight results, which average O=15.9733; ± .0113. The general mean from both investigations is

$$O=15.9642\ ;\ \pm .006.$$

The density of hydrogen, referred to air as unity, was determined by Regnault in three experiments. The mean was .069263; ± .000019. For oxygen four determinations were made by Regnault, and one of them was rejected. The three remaining figures give a density of 1.105633; ± .000008. The ratio between these two density estimations gives an atomic weight of

$$O=15.9628\ ;\ \pm .0044.$$

Combining this with the value found from the synthesis of water, we get a general mean of

$$O=15.9633\ ;\ \pm .0035.$$

This is the most probable value which can be deduced from the published data; and it forms the corner-stone upon which our entire system of atomic weights must rest. I need not discuss here the methods employed in the calculation of probable errors, for they are given in all treatises upon least squares. Suffice it to say that I assign no arbitrary weights to the values under examination. Each series of experiments receives the weight to which the probable error of its mean entitles it.

Having found a value for oxygen, I next discussed in a group the atomic weights of the elements chlorine, bromine, iodine, silver, potassium, sodium and sulphur. The data to be considered were determined by Berzelius, Penny, Pelouze, Marignac, Maumené, Gerhardt, Millon, Struve, Svanberg and Struve, Turner, Dumas, Cooke, and Stas; and represented twenty distinct ratios. For example, one of the most important ratios was that between potassium chloride and potassium chlorate; for which there were nine series of determinations. The mean of each series was calculated, together with its probable error, and then all nine means were combined into one general mean. Thus all the available data were reduced to the twenty compact ratios above referred to. Two of these may be cited to illustrate the methods of calculation.

1. Percentage of O in $KClO_3$, 39.154; $\pm$ .0004.
2. Ag : KCl : : 100 : 69.1032; $\pm$ .0002.

From the first of these ratios the molecular weight of KCl is easily calculated by the usual proportion, 39.154 : 60.846 : : O_3 : x. Using the value for oxygen previously found, x, or KCl, becomes 74.4217; and as the probable errors are known for the three known terms of the proportion, we easily deduce that of the fourth term, and write

$$KCl = 74.4217;\ \pm .0164.$$

Here the probable error is a function of the probable errors of the experiments upon potassium chlorate, and the probable error of the atomic weight of oxygen. We may now use this value for KCl in connection with the second of the ratios above cited, and deduce for the atomic weight of silver the figure

$$Ag = 107.696;\ \pm .024.$$

In every proportion used there are known probable errors for three terms, and they are involved in the probable error of the fourth term. From the twenty ratios above referred to, eight entirely independent values for the atomic weight of silver can be found. Each value has a definitely ascertained probable error, and each receives the weight which that error indicates. The general mean of all is

$$Ag = 107.675;\ \pm .0096.$$

This is the final result from the discussion of over two hundred experiments; and it gives us the key to the atomic weights of the

other elements in the group under consideration. These are as follows, when O=15.9633; ± .0035.

Cl = 35.370; ± .014
Br = 79.768; ± .019
I = 126.557; ± .022
K = 39.019; ± .012
Na = 22.998; ± .011
S = 31.984; ± .012

The values which Stas assigns to these elements are all based upon the standard of O=16. If we adapt the above figures to the same standard, we may compare them side by side with those of Stas. As the latter chemist also determined the atomic weights of nitrogen, lithium and lead, I will include the values found in this recalculation for these substances also.

ATOMIC WEIGHTS WITH O=16.

	New Values.	Stas' Values.	Difference.
Ag	107.923	107.930	— .007
Cl	35.451	35.457	— .006
Br	79.951	79.952	— .001
I	126.848	126.850	— .002
Na	23.051	23.043	+ .009
K	39.109	39.137	— .028
S	32.058	32.074	— .016
N	14.029	14.044	— .015
Li	7.0235	7.022	+ .0015
Pb	206.946	206.926	+ .020

The magnificent accuracy of Stas' manipulations could hardly receive more striking confirmation than is afforded by these figures.

The atomic weights of the remaining elements I give below, in the order of their calculation. I also give the authorities whose experiments are combined in the values presented. Elaborate details there is of course no room for; they must be sought in the complete monograph when the latter is published.

Nitrogen. Data by Regnault, Pelouze, Marignac, Turner, Penny, and Stas. General mean of all, N=14.0210; ± .0035. This value involves the values previously found for O, K, Na, Ag and Cl.

Carbon. Data by Liebig and Redtenbacher, Maumené, Dumas and Stas, Erdmann and Marchand, and Stas. General mean of all, $C = 12.0021$; $\pm .0019$. Rejecting the series by Liebig and Redtenbacher and by Maumené, which involve constant errors, we get from the remaining series a value of $C = 11.9736$; $\pm .0028$. If $O = 16$ this becomes $C = 12.0011$. The ratio between oxygen and carbon therefore is a ratio between two whole numbers, 16 and 12.

Barium. Determined by Berzelius, Turner, Struve, Pelouze, Marignac, Dumas, and Stas. General mean, $Ba = 136.763$; $\pm .031$. If $O = 16$, $Ba = 137.007$.

Strontium. Data by Pelouze, Dumas, and Marignac. General mean, $Sr = 87.374$; $\pm .032$.

Calcium. Experiments by Berzelius, Erdmann and Marchand, and Dumas. $Ca = 39.990$; $\pm .010$. The best single result by Erdmann and Marchand gives $Ca = 39.905$; or, if $O = 16$, $Ca = 39.997$.

Lead. Berzelius, Turner, Marignac, Dumas, Anderson, and Stas. Some data were rejected. The final most probable value is $Pb = 206.471$; $\pm .021$.

Fluorine. Berzelius, Louyet, Dumas, and DeLuca. General mean, $F = 18.984$; $\pm .007$.

Phosphorus. The only good determinations for this element are those by Schrötter and by Dumas. General mean of both series, $P = 30.958$; $\pm .007$.

Boron. Berzelius, Laurent, Dumas and Deville. In mean, $B = 10.941$; $\pm .023$. Not well determined.

Silicon. Pelouze, Dumas, and Schiel. $Si = 28.195$; $\pm .031$ This constant needs thorough experimental revision.

Lithium. Mallet, Diehl, Troost, and Stas. General mean, $Li = 7.0073$; $\pm .007$.

Rubidium. Bunsen, Piccard, Godeffroy. $Rb = 85.251$; $\pm .0045$.

Caesium. Johnson and Allen, Bunsen, and Godeffroy. $Cs = 132.583$; $\pm .024$.

Thallium. Although I have recalculated the results obtained by Lamy, Hebberling, and Werther, I need consider here only the experiments of Crookes. His weighings, calculated with the values for O and N given above, make $Tl = 203.715$; $\pm .037$. Crookes himself, using the value $NO_3 = 61.889$, found $Tl = 203.642$, and regards his results as evidence against Prout's hypothesis. His experiments, however, really fix only the ratio between NO_3 and

Tl. If $NO_3=62$, then $Tl=204.008$. That is, the ratio which Crookes has rigorously established is a ratio between two whole numbers, and is confirmatory of Prout's idea.

Glucinum. The results of Awdejew, Klatzo, Weeren, and Debray, have high probable errors, and practically vanish from the mean when combined with those of Nilson and Pettersson. The weighings published by the latter chemists give me $Gl=9.085$; $\pm$ .0055; or $Gl=13.628$; $\pm$ .008; according to whether the oxide is GlO or Gl_2O_3.

Magnesium. Scheerer, Svanberg and Nordenfeldt, Bahr, Jacquelain, Marchand and Scheerer, and Dumas. General mean of all, $Mg=24.103$; $\pm$ .004. Some of the series are vitiated by constant errors. The best value is to be deduced from Marchand and Scheerer's work alone, and is $Mg=23.959$; $\pm$ .005.

Zinc. Jacquelain, Favre, and Axel Erdmann. General mean, $Zn=65.557$; $\pm$ .011. Erdmann's results alone, however, give a more probable value (considered chemically) of $Zn=64.9045$; $\pm$ .019.

Cadmium. Von Hauer, Lenssen, and Dumas. General mean, $Cd=111.770$; $\pm$ .030.

Mercury. Part of Turner's data are to be considered, together with results by Erdmann and Marchand, Millon, and Svanberg. General mean, $Hg=199.712$; $\pm$ .042. New determinations are much needed.

Chromium. Peligot's work was not available for discussion. The data studied were by Berlin, Moberg, Lefort, Wildenstein, Kessler, and Siewert. General mean from all, $Cr=52.453$; $\pm$ .015. Berlin's work, considered by itself, gives $Cr=52.389$; $\pm$ .019. Siewert's results give $Cr=52.009$; $\pm$ .025. I regard the last value as freest from constant errors, and use it in subsequent calculations.

Manganese. Turner, Berzelius, Dumas, v. Hauer, Schneider, and Rawack. General mean, $Mn=54.128$; $\pm$ .011. Schneider's and Rawack's results give a better value of $Mn=53.906$; $\pm$ .012.

Iron. Berzelius, Svanberg and Norlin, Erdmann and Marchand, Maumené, Rivot, and Dumas. General mean, $Fe=55.913$; $\pm$ .012.

Copper. Berzelius, Erdmann and Marchand, Millon and Commaille, and Hampe. $Cu=63.173$; $\pm$ .011.

Molybdenum. Debray, Dumas, Rammelsberg, and analyses by Liechti and Kemp. $Mo=95.527$; $\pm$ .051.

Tungsten. Berzelius, Schneider, Marchand, v. Borch, Dumas, Bernoulli, Persoz, Roscoe, Scheibler, and Zettnow. General mean of all, $W=183.610$; $\pm .032$.

Uranium. Peligot, Ebelmen, and Wertheim. General mean, $U=238.481$; $\pm .082$.

Aluminum. Berzelius, Tissier, Isnard, Dumas, Terreil, and Mallet. General mean, $Al=27.0092$; $\pm .0028$. All the data except Mallet's might be rejected without essentially affecting this value.

Gold. Berzelius, and Levol. $Au=196.155$; $\pm .095$. A thorough redetermination is much needed.

Nickel. Several early series for nickel and cobalt were rejected. The data taken were by Schneider, Dumas, Russell, Sommaruga, Winkler, and Lee. General mean, $Ni=58.547$; $\pm .009$. I attach more importance to the concordant results of Schneider, Sommaruga, and Lee, whose figures give a general mean of $Ni=57.928$; $\pm .022$, Lee's investigation was of all the least susceptible to constant errors.

Cobalt. Schneider, Dumas, Russell, Sommaruga, Winkler, Weselsky, and Lee. $Co=58.887$; $\pm .008$.

Selenium. Berzelius, Sacc, Erdmann and Marchand, Dumas, and Ekman and Pettersson. $Se=78.797$; $\pm .011$.

Tellurium. Berzelius, v. Hauer, and Wills. General mean, $Te=127.960$; $\pm .034$. The results of v. Hauer and Wills upon K_2TeBr_6 give $Te=127.170$; $\pm .173$. Wills' minimum figures give me $Te=126.07$. In all of these results certain constant errors are possible; so that the question raised by Mendelejeff as to whether tellurium is above or below iodine, cannot be regarded as settled.

Vanadium. Roscoe's weighings, recalculated with the new values for O, Ag, and Cl, give $V=51.256$; $\pm .024$.

Arsenic. Pelouze, Dumas, Wallace, and Kessler. General mean, $As=74.918$; $\pm .016$: Wallace's analyses of $AsBr_3$ were made to establish the atomic weight of bromine, but they serve a better purpose here.

Antimony. For this element there have been the two rival figures 120 and 122. The general mean from data by Kessler, Dumas, and Dexter, is $Sb=122.092$; $\pm .035$. The general mean from the experiments of Schneider and of Cooke is $Sb=119.955$; $\pm .036$. In view of the recent discussions upon the subject, we may regard the lower figure as established.

Bismuth. General mean from Schneider's experiments, Bi=207.523; ± .082. If O=16, this becomes 208.001. All of Dumas' results on bismuth chloride give a mean of Bi=210.464; the figures which he considers best give Bi=209.78. Schneider's work is probably nearest correct, his method being less liable to constant errors than that of Dumas.

Tin. Berzelius, Mulder and Vlaanderen, Dumas, and Vlaanderen. General mean, Sn=117.698; ± .040.

Titanium. Rose's weighings give Ti=48.710; ± .105. Mosander's figures give Ti=47.045. Pierre's give Ti=49.889; ± .096; and Demoly's, Ti=52.191; ± .153. A general mean of the results of Pierre, Rose, and Demoly is 49.846; ± .064. Mosander's work must be rejected, for want of sufficient details. An experimental revision is wanted.

Zirconium. From Berzelius' figures Zr=89.255; ± .039. From Marignac's data Zr=90.328; ± .113. The general mean of both sets is Zr=89.367; ± .037. New determinations are evidently needed.

Thorium. Berzelius, Chydenius, Berlin, Delafontaine, Hermann, and Cleve. General mean, Th=233.414; ± .073.

Gallium. From Boisbandran's results, in mean, Ga=68.854.

Indium. Reich and Richter, Winkler, and Bunsen. General mean, In=113.398; ± .047.

Cerium. Beringer, Hermann, Marignac, Bunsen and Jegel, Rammelsberg, Wolf, Wing, and Buehrig. General mean of all, Ce=140.424; ± .017. Buehrig's analyses of the oxalate give Ce=141.198; ± .020. The figures by Wolf and by Wing give Ce=137.724. Wolf and Wing had a *white* ceroso-ceric oxide, and Wolf suspects the ordinary yellowish compound to contain a fourth metal of the cerium group. Buehrig's work is the best, but the possible presence of a fourth metal is not considered by this chemist. Therefore new experiments are needed.

Lanthanum. Hermann, Rammelsberg, Marignac, Czudnowicz, Holzmann, Zschiesche, Erk, and Cleve. General mean, La=138.526; ± .030.

Didymium. Marignac, Hermann, Zschiesche, Erk, and Cleve. General mean, Di=144.573; ± .031. Cleve's work alone, which is doubtless the best, gives Di=146.804.

Scandium. Nilson's results, recalculated, give Sc=43.980; ± .015.

Yttrium. Popp, Delafontaine, Bahr and Bunsen, and Cleve. General mean, Yt=97.616. Excluding Popp's work as worthless, the general mean becomes Yt=89.816; ± .067.

Ytterbium. Nilson. Yb=172.761; ± .038.

Erbium. For this metal the most probable results are those of Cleve, which give, recalculated, Er=165.891. Previous workers undoubtedly studied material rich in ytterbium and other metals of the group.

For terbium, samarium, phillipium, decipium, thulium, etc., there are no satisfactory data. Cleve gives 170.7 for thulium, while Delafontaine puts Ph=123 to 125, and Dp=171. These figures assume that all the earths of the group are sesquioxides.

Columbium.[1] Marignac's results give approximately Cb=94. Blomstrand regards 95 as the most probable value. New estimations are needed.

Tantalum. All of Marignac's figures give a general mean of Ta=182.144; ± .166. Probably 182 may be safely used as the true value.

Platinum. By a recalculation of the results lately published by Seubert, I get Pt=194.415; ± .049.

Osmium. Berzelius' figures give me Os=198.494.

Iridium. The general mean calculated from Seubert's weighings is Ir=192.651; ± .033.

Palladium. Berzelius' last results are the only ones worth considering. They give Pd=105.737.

Rhodium. Data by Berzelius. Rh=104.055.

Ruthenium. A single analysis of potassium rutheniochloride by Claus gives Rh=104.217. Plainly, the values for Ru, Rh, Pd, and Os need scrupulous redetermination.

Conclusions.

A careful scrutiny of all the data upon which the foregoing atomic weight calculations depend, will reveal various sources of error. Of course, each series of results must be considered by itself, and weighed on its own merits; but a few general errors are important enough to warrant mention here.

[1]This name has priority over the generally accepted "niobium," and therefore is entitled to preference.

First, every value after oxygen, with one or two partial exceptions, involves whatever error may attach to the atomic weight of oxygen. If the latter is 16, instead of 15.9633, this error in some instances becomes multiplied to a serious extent, as a glance at the tabulated results will show. Other similar errors are repeated continually. The value assigned to any element is necessarily affected by whatever errors may attach to the atomic weights of those other elements through whose medium it is referred to the standard, hydrogen.

Secondly, confusion arises from the fact that many of the weighings under discussion were not reduced to the standard of a vacuum, while others had been subjected to such a correction. The errors thus introduced into the calculations are small, but still they cannot be lost sight of.

Another set of errors of unknown magnitude are produced as follows. Many series of experiments, notably in the work of Stas, Marignac, and other eminent investigators, involve the titration of chlorides, bromides, or iodides with solutions containing known weights of metallic silver. But Dumas has lately shown that silver purified after the usual methods occludes weighable quantities of oxygen. In other words, the silver hitherto employed in atomic weight investigations has not been pure silver. One exception is found in Mallet's research upon aluminum. Since the atomic weights of nearly all the elements depend directly or indirectly upon silver, this source of error becomes of the greatest importance. Analogous errors may possibly occur with metals other than silver, and should be carefully looked for. For example, the atomic weights of both copper and oxygen depend upon the reduction of copper oxide in hydrogen. If the residual copper, which is weighed, occludes any hydrogen, then the atomic weight of copper will come out too high, and that of oxygen a trifle too low. Such an error might account for the difference between 15.9633 and 16 in the case of oxygen.

In connection with the data discussed in this investigation it is perhaps worth while to consider the bearing of the results upon Prout's famous hypothesis. In order to simplify matters I tabulate the new atomic weight values in two columns; one containing numbers referred to hydrogen as unity, the other with figures comparable with oxygen as equal to sixteen.

TABLE OF ATOMIC WEIGHTS.

	H=1.	O=16.		H=1.	O=16.
Hydrogen,	1.0000	1.0023	Sodium,	22.998	23.051
Fluorine,	18.984	19.027	Potassium,	39.019	39.109
Chlorine,	35.370	35.451	Rubidium,	85.251	85.529
Bromine,	79.768	79.951	Caesium,	132.583	132.918
Iodine,	126.557	126.848	Silver,	107.675	107.923
Lithium,	7.0073	7.0235	Thallium	203.715	204.183
Glucinum,	9.085	9.106	Phosphorus,	30.958	31.029
Magnesium,	23.959	24.014	Vanadium,	51.256	51.373
Zinc,	64.905	65.054	Arsenic	74.918	75.090
Cadmium,	111.770	112.027	Antimony,	119.955	120.231
Mercury,	199.712	200.171	Bismuth,	207 523	208.001
Calcium,	39.990	40.082	Columbium,	Ab't 94.	Ab't 94.
Strontium,	87.374	87.575	Tantalum,	182.144	182.562
Barium,	136.763	137.007	Scandium,	43.980	44.081
Lead,	206.471	206.946	Yttrium,	89.816	90.023
Oxygen,	15.9633	16.0000	Erbium,	165.891	166.273
Sulphur,	31.984	32.074	Ytterbium,	172.761	173.158
Selenium,	78.797	78.978	Cerium,	140.424	140.747
Tellurium,	127.960	128.254	Lanthanum,	138.526	138.844
Chromium,	52.009	52.129	Didymium,	144.573	144.906
Molybdenum,	95.527	95.747	Carbon,	11.9736	12.0011
Tungsten,	183.610	184.032	Silicon,	28.195	28.260
Uranium,	238.482	239.030	Titanium,	49.846	49.961
Manganese,	53.906	54.029	Zirconium,	89.367	89.573
Iron,	55.913	56.042	Tin,	117.698	117.968
Nickel,	57.928	58.062	Thorium,	233.414	233.951
Cobalt,	58.887	59.023	Platinum,	194.415	194.867
Copper,	63.173	63.318	Iridium,	192.651	193.094
Boron,	10.941	10.966	Osmium,	198.494	198.951
Aluminum,	27.009	27.075	Palladium,	105.737	105.981
Gallium,	68.854	68.963	Rhodium,	104.055	104.285
Indium,	113.398	113.659	Ruthenium,	104.217	104.457
Nitrogen,	14.021	14.029	Gold,	196.155	196.606

Here we have sixty-six elements, or rejecting columbium as too vaguely determined, sixty-five. Such elements as phillipium, decipium, thulium, samarium, etc., are not yet sufficiently well known to be considered in this connection.

In his recent superb investigation of the atomic weight of aluminum, Mallet makes substantially the following argument in favor of Prout's hypothesis. Considering the atomic weights of eighteen elements only as well determined, he finds that ten of them have values varying less than 0.1 from whole numbers. In other words, these ten elements have atomic weights varying from even multiples of that of hydrogen by insignificant amounts. What is the probability that this agreement with Prout's hypothesis in ten cases out of eighteen is purely accidental, as those hold who agree with the views of Stas? Working this problem out he finds the probability of mere coincidence to be 1 : 1097.8, and he concludes that Prout's hypothesis is still worthy of careful consideration.

Applying Mallet's reasoning to the table of atomic weights now before us, we find that in the first column, when H = 1, twenty-five out of sixty-five elements have atomic weights falling within one-

tenth of a unit of whole numbers. But many of the figures which fall outside this limit of variation involve the variation of oxygen multiplied many times over. We must, therefore, study the second column which assumes $O=16$. Here we have thirty-nine elements falling within the limit of variation assigned by Mallet, and twenty-six falling without. The latter are chlorine, iodine, potassium, thallium, glucinum, mercury, strontium, tellurium, chromium, molybdenum, rubidium, copper, indium, vanadium, antimony, tantalum, erbium, ytterbium, cerium, lanthanum, silicon, zirconium, platinum, rhodium, ruthenium, and gold. Of these, chlorine, rubidium and strontium agree closely with half multiples of hydrogen; while tellurium, molybdenum, indium, tantalum, erbium, cerium, silicon, zirconium, lanthanum, rhodium and ruthenium may be dismissed from consideration as not sufficiently well determined to bear upon the problem before us. The exceptions in the cases of potassium, iodine, thallium, glucinum, mercury, chromium, vanadium, antimony, ytterbium, platinum and gold, remain to be considered.

For potassium and iodine, we must remember that both of these elements involve the constant error due to the occlusion of oxygen by silver. This error is probably great enough to throw the values for both elements outside the limit of variation above assigned. For thallium, it has already been shown that when its atomic weight is calculated with $NO_3=62$, Crookes' data give $Tl=204.008$. The atomic weights of glucinum and ytterbium, as given in the tables, are calculated from analyses of the sulphates. If $SO_3=80$, then $Gl=9.096$, and $Yb=173.016$. Both fall within, and one *narrowly* within the limit of one-tenth of a unit variation. In the case of platinum I need only say that Seubert's figures give values ranging both above and below the even number 195; while as for antimony, although the general mean is $Sb=120.231$, Cooke's analyses of the bromide, reckoned with $Br=80$, give almost exactly 120 for the value. For mercury, chromium, vanadium and gold, new determinations are desirable.

Enough has been said to show that none of the apparent exceptions to Prout's hypothesis are absolutely inexplicable. As the figures actually stand, thirty-nine out of sixty-five elements vary less than a tenth of a unit each from even multiples of the atomic weight of hydrogen. Of the remaining twenty-six, three conform to half multiples, three more are legitimately recalculable so as to

fall within bounds, and eleven have been so defectively determined that the assigned values can carry scarcely any weight. The remaining nine are still subject to slight revision. In short, the many agreements, which include three-fourths of the *well* determined atomic weights, render Prout's hypothesis very highly probable. It is more likely that the seeming exceptions are due to undetected constant errors, than that the great number of coincidences should be accidental. The mathematical probability in favor of Prout's hypothesis I have not yet calculated, but a glance at Mallet's figures will show that it must be enormous.

As I said at the beginning, this paper is but a summary of methods and conclusions. Within its scope, elaborate discussions would not be admissible. I hope that my complete memoir will soon be published; and it is my intention to discuss, in an appendix to it, both the bearing of the results upon Prout's hypothesis, and the distribution of the variations therefrom. I ought to say that at the beginning of my investigation I was strongly prejudiced against Prout's hypothesis, and fully believed that it had been forever overthrown. My results have forced me to give it very respectful consideration.

METHOD FOR ACCURATE AND RAPID ANALYSES OF AIR.

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I have made a series of daily analyses in duplicate of air collected at this place for six months beginning with January 1, 1880, and one for six months and twenty days, beginning October 1, 1880. The samples of air were collected in bottles with well fitting glass stoppers. A few drops of solution of potassium hydrate being put into the bottle, this was set in the open air, and the air in the bottle displaced by sufficient aspiration, the observer keeping at a little distance to the leeward side. The stopper was then put in place and wet with the potassium hydrate by inverting the bottle and turning the stopper. Experiment showed that it was possible to keep samples for many days in this way with the certainty that they remained unchanged.

A mercury pump was used to withdraw the sample from the bottle. A rubber stopper was used to make the needed connection with the pump. Experiment showed that this rubber in contact with the alkaline solution does not absorb more than a hundredth per cent. of oxygen from the air in the bottle in twenty times the period during which it was in contact with the air used in the analysis. The pump discharged the air into a jar standing over mercury in the laboratory trough of the apparatus for analysis.

This jar being lowered, together with the cistern, over the recurved capillary end of the eudiometer tube, a certain quantity of air was taken into this tube. This quantity was measured approximately by using a journeyman pressure tube having a small bore. The quantity used was almost always the same, and occupied from 470 to 475 millimetres in length of the eudiometer tube, when the pressure on it was that of a column of mercury of this same length.

This quantity was then measured accurately with the standard pressure tube. This had a Jolly point in the vacuum at the level of the zero of the graduation on the eudiometer tube, which zero was at the top of the tube. The level of the mercury in the standard pressure tube being never permitted to vary more than a fraction of a millimetre, its vacuum was found to remain constant and unimpaired. When the mercury in it had been put in connection with the mercury in the eudiometer, and its upper level had been brought to the Jolly point by the use of a fine adjustment, the level of the mercury in the eudiometer was read with a microscope magnifying fifty diameters, and provided with an eye-piece micrometer. By this arrangement, when everything was prepared, it was possible to verify the contact at the Jolly point, to read the thermometer to the hundredth of a degree, and to read the level of the mercury in the eudiometer, in less than ten seconds. Uncertainty as to the actual temperature at the instant of final reading was in this way mostly avoided. This reading microscope is carried on a vertical cylinder which is solidly attached to the firm iron tripod which supports the whole apparatus. On this cylinder the mounting of the microscope can be clamped at the required height. The microscope is then made to give distinct vision of the graduation on the surface of the eudiometer. This graduation consists of lines not more than the eight thousandth of an inch wide, cut with a diamond. No errors exist amounting to the hundredth of a millimetre in the parts of the

graduation which have been used in these analyses. When distinct vision is obtained of the graduation, a fine adjustment moves the microscope vertically till the terminal lines of the eye-piece micrometer coincide with two lines of the graduation on the eudiometer. If now the horizontal focusing movement carries the microscope forward about half an inch towards the eudiometer, the microscope will give distinct vision of the meniscus in the tube, and its level can be read by the divisions of the eye-piece micrometer, which represent the divisions on the surface of the tube carried forward optically into its interior. It would be easy to show how far the use of such an arrangement is superior to that of a cathetometer for the purpose in hand, in accuracy, in rapidity, and in simplicity of reduction for expansion of the scale.

The measured quantity of air was next transferred to a jar standing over mercury in the laboratory trough.

A quantity of hydrogen amounting to about sixty-three per cent. of the air taken was next measured approximately, and added to the air in the jar. This amount was always the same, so that any errors which were a function of the quantity of hydrogen should be constant in amount, and should not therefore affect the *differences* of the analyses. Sixty-three per cent. was used in order that the last and first readings of volume might be made with the same position of the reading microscope.

After the air and hydrogen had had time thoroughly to mix, they were transferred back to the eudiometer, measured, expanded, exploded, and again measured. The expansion was always the same. In the transfers mentioned there is absolutely no possibility of loss or of admixture by leakage except by gross carelessness. The only place where leakage could take place is the stop-cock at the top of the eudiometer. This stop-cock was specially made for this place, and has not yet been found to leak, though it has been tested for ten minutes against an internal vacuum before or after each analysis.

Two coincident readings were obtained for each measurement, though the result was always calculated from the last reading. To secure accurate determinations of temperature, the eudiometer and pressure tubes are enclosed in a box with plate-glass front and back, containing about ten litres of distilled water. This is vigorously stirred, except at the instant of reading the microscope, by means of a current of air from a condensing pump driven by power. I

have had no difficulty in getting the required two coincident readings in half a minute when the thermometer was rising; but when the thermometer is falling, the difficulty in getting a reading of the thermometer which shall really represent the temperature is enough to make work very vexatious, for an error of a hundredth of a degree in the difference of temperature at two measurements in the same analysis is close upon the limit of allowance.

Great care has been taken to obtain hydrogen of sufficient purity. In the early analyses, a Bunsen's decomposing cell of the common form was used. It then often happened that the analysis made with the first hydrogen obtained after an interval of rest would give results showing a deficiency of oxygen of about a hundredth of one per cent. Often analyses had to be rejected, until the cell was freed from compounds of hydrogen with zinc or carbon, which had been produced by local action at the surface of the zinc. Finally, a cell was constructed which could be every morning connected with the air-pump and exhausted of hydrogen, so as to remove these compounds of hydrogen with zinc or carbon, whether they had risen through the liquid, or were still adherent to the zinc plate or dissolved in the dilute acid. The cell had a mercury stop-cock which interposed a barometric column against the leakage of air into the cell; but for additional security, the hydrogen coming from it passed through several inches of active platinum black. In this way I have now secured a supply of hydrogen which probably never occasions a difference of a five hundredth of one per cent. in two analyses of the same sample. Experiment shows that hydrogen may safely be left standing over mercury in a *clean* bell-glass for a long time. I have left two samples for eleven weeks, which samples then were used in a duplicate analysis of a sample of air against a duplicate analysis of the same sample made with two samples of hydrogen just from the decomposing cell. Hydrogen was therefore sometimes used which had stood for a few days. Duplicate analyses were always made with different samples of hydrogen.

It may be observed that the corresponding measurements of different analyses were made under identical conditions. The calibration error, and the error caused by the imperfect parallelism of the reading microscope in its different positions, therefore, disappear from the *differences* of the analyses of different samples. The same is true of the error caused by the production of water in the

eudiometer between the second and third measurements in each analysis. No correction has been applied for this error, because the distribution of the water above and below the meniscus can not be easily determined. The amount of water adhering to the interior of the eudiometer before the commencement of an analysis has also been made always approximately the same. This has been accomplished by producing a vacuum in the eudiometer after the analysis, and the letting the mercury rise in it with a determinate velocity; when the eudiometer is clean, considerable uniformity is thus obtained.

In making observation as accurate as is required for my purpose, it is very important to keep the interior of the eudiometer very clean. A little irregularity in the film of water through which the meniscus is seen will spoil the reading. My eudiometer tube is cemented into a brass fitting which rests in a seat ground for it in the bottom of the enveloping box mentioned before. The eudiometer can be disconnected, removed, washed with caustic potash and shot, rinsed out with dust-free distilled water, and replaced ready for analysis, in an hour. The accurate fitting of the ground seat makes it possible to restore the zero of the graduation on the tube to the same level within the two hundredth of a millimetre, without even the bestowal of any thought on the matter. With this facility, the eudiometer has been kept sufficiently clean for accurate reading.

It is of course possible that the mean of all my analyses with the new apparatus is affected with a measurable constant error, though no measurable error has yet been traced to any assignable source. But it is certain that the differences in the means for different periods are affected with but very small errors. During the most favorable conditions under which I have used the apparatus, taking seventy minutes for each pair of analyses of the same sample, the mean error of a single analysis was, for half a month, less than the thousandth part of one per cent. Having commonly to work at odd times, and more rapidly than this, the accuracy attained has been less; but, for the whole seven hundred and eighty-eight analyses made with it, the mean error of a single analysis has been less than the two hundred and eightieth of one per cent. If, then, two samples of air differ by one-fiftieth of one per cent. in their contents of oxygen, the fact of a difference can be detected with a degree of probability nearly approaching certainty, at an expenditure of time not exceeding one hour for each sample.

NOTICE OF A PHOSPHORUSOXYIODIDE.

BY BEVERLY S. BURTON.

Having frequently observed, on closely examining the residue in the retort after preparing ethyl iodide, minute golden scales, I was induced to examine these more closely. To this end the residue was treated with water and filtered from the excess of red phosphorus ; the filtrate was then evaporated on the water-bath.

When quite concentrated, and allowed to cool, a quantity of granular red crystals was deposited, which were purified by drying on filter paper and recrystallization until all free iodine was perfectly removed. On one occasion the crystals were obtained much larger, with brilliant facets; the form was not determined. It is very soluble in water, alcohol and ether, the solution being perfectly colorless. This property is made peculiarly striking when the dish is simply wet with the solution and placed on the water-bath, thus becoming almost instantly a deep orange color to a beautiful scarlet, which again disappears when held a moment in the steam.

On heating, the crystals melt to a deep reddish brown crystalline mass ; the melting point being 140°.

By increasing the heat, yellowish vapors are given off which blue starch-paper. These vapors condense on a cold surface as a yellowish red crystalline deposit, which behaves in all respects as the original body, *i. e.* sublimes, in part, unaltered.

The portions used in the further examination were purified perfectly from all free iodine and dried over sulphuric acid. It being found that a solution of the body was completely decomposed by silver nitrate, the method of analysis was the following :

An excess of silver nitrate was added to the solution, the separated silver iodide filtered off, and the excess of silver in the filtrate separated by hydrochloric acid. To the filtrate, free from silver, an excess of sodium carbonate was added, also a little sodium nitrate, then the whole evaporated to dryness and fused. The solution of the fused mass then precipitated with magnesia mixture ; any alumina or silica, which might separate on addition of ammonia, being previously removed.

The following results were obtained :

	I.	II.
I	77.93	77.44
P	9.66	9.71
O	12.41	12.85
	100.00	100.00

corresponding to the formula $I_6P_3O_8$. On one occasion this body was also observed in the residue from the preparation of fuming hydriodic acid; it was extracted, purified, and the analysis made as above described, yielding the following:

I	81.91	81.88
P	8.36	8.22
O	9.73	9.90
	100.00	100.00

corresponding to I_2PO_2, or for better comparison with the above, $I_8P_4O_8$.

As it was considered not improbable that hydrogen might enter into its composition, a combustion was made, the substance being introduced in a boat before which was laid copper oxide, a long layer of lead chromate and a silver spiral, but the amount found was too minute to be regarded.

I would mention here that in the preparation of methyl iodide the same body is apparently formed; but on attempting to purify in the same manner, a brown residue remained on treating with water. This was filtered off, and on evaporating the filtrate the crystals before noticed were not formed, but yellow flocks resembling freshly precipitated arsenic sulphide separated, which behaved very differently from that previously obtained.

An attempt to prepare this compound was made by leading phosphine gas evolved by the action of water upon phosphonium iodide, into a solution of iodine in hydriodic acid, but so far without success. Owing to the very small quantities at disposal, and the want of a method of preparation, its more exact constitution cannot be given. As at present no definite formula seems to be indicated, any speculations as to the nature of this body, or whether possibly two or more exist, are premature.

Its further study will be continued at the earliest opportunity.

REVIEWS AND REPORTS.

ARTIFICIAL INDIGO.

Though the chemical processes involved in the artificial production of indigo have already been brought before the attention of the readers of this Journal, the following extracts from a lecture by Professor Roscoe, delivered before the Royal Institution of Great Britain, will not be without interest, as a number of facts connected with the industry of dyeing with the artificial dye-stuff are made public for the first time in the lecture.

After speaking of the discovery of indigo and the methods used for extracting the dye-stuff from the plant, the lecturer recounts the steps which have led to the discovery of the constitution of indigo, and consequently to its synthesis. These are:

STEP NO. 1.—This was made so long ago as 1840, when Fritsche proved that aniline, $C_6H_5NH_2$, can be obtained from indigo. The name for this now well-known substance is indeed derived from the Portuguese "anil," a word used to designate the blue color from indigo. This result of Fritsche's is of great importance, as showing that indigo is built up from the well-known benzene ring C_6H_6, the skeleton of all the aromatic compounds, and, moreover, that it contains an amido-group.

STEP NO. 2 was also made by Fritsche in the following year, when, by boiling indigo with soda and manganese dioxide, he obtained ortho-amido-benzoic acid, or, as he then termed it, anthranilic acid. The following is the reaction which here occurs:

$$\underset{\text{Indigo.}}{C_8H_5NO} + O + 2H_2O = \underset{\substack{\text{Ortho-amido-}\\\text{benzoic acid.}}}{C_7H_5NH_2O_2} + \underset{\substack{\text{Formic}\\\text{acid.}}}{CH_2O_2}$$

What light does this fact shed upon the constitution of indigo? It shows (1) that one of the eight atoms of carbon in indigo can be readily separated from the rest; (2) that the carboxyl and the amido-group are in neighboring positions in the benzene ring, viz. 1 and 2.

STEP NO. 3.—The next advance of importance in this somewhat complicated matter, is the discovery by Erdmann and Laurent independently, that indigo on oxidation yields a crystalline body, which, however, possesses no coloring power, to which they gave the name isatin.

$$\underset{\text{Indigo.}}{C_8H_5NO} + O = \underset{\text{Isatin.}}{C_8H_5NO_2}$$

STEP No. 4.—The reverse of this action, viz., the reduction of isatin to indigo, was accomplished by Baeyer and Emmerling in 1870 and 1878, by acting with phosphorus pentachloride on isatin, and by the reducing action of ammonium sulphide on the chloride thus formed.

Understanding now something of the structure and of the relationships of the body which we wish to build up, let us see how this edifice has, in fact, been reared. Three processes have been successfully employed for carrying out this object. But of these three only one is of practical importance.

For the sake of completeness, let us, however, consider all three processes, although Nos. 1 and 2 are at present beyond the pale of practical schemes.

These three processes have certain points in common. (1) They all proceed from some compound containing the benzene nucleus. (2) They all start from compounds containing a nitrogen atom. (3) They all commence with an ortho-compound.

They differ from one another, inasmuch as No. 1 starts from a compound containing 7 atoms of carbon (instead of 8), and to this, therefore, one more atom must be added; process No. 2, on the other hand, starts from a body which contains exactly the right number (8) of carbon atoms; whilst No. 3 commences with a compound in which 9 atoms of carbon are contained and from which, therefore, 1 atom has to be abstracted before indigo can be reached.

Process No. 1 (Kekulé, Claissen and Shadwell).—So long ago as 1869 Kekulé predicted the constitution of isatin, and gave to it the formula which we now know that it possesses, viz.:

$$C_6H_4\left\langle\begin{array}{c}CO\\NH\end{array}\right\rangle CO.$$

Following up this view, Claissen and Shadwell, two of Kekulé's pupils, succeeded in preparing isatin, and, therefore, now indigo from ortho-nitro-benzoic acid.

The following are the steps in the ascent:

1. Ortho-nitro-benzoic acid acted on by phosphorus pentachloride yields the chloride $C_6H_4(NO_2)COCl$.

2. This latter heated with silver cyanide yields the nitril $C_6H_4(NO_2)CO.CN$.

3. On heating this with caustic potash it yields ortho-nitro-phenyl-glyoxylic acid, $C_6H_4(NO_2)CO.CO_2H$.

4. This is converted by nascent hydrogen into the amido-compound $C_6H_4(NH_2).CO.CO_2H$.

5. And this loses water and yields isatin, $C_6H_4NH.CO.CO$. (*Q. E. D.*)

The reasons why this process will not work on a large scale are patent to all those who have had even a bowing acquaintance with such unpleasant and costly bodies as phosphorus pentachloride or cyanogen.

Process No. 2.—Baeyer's (1878) synthesis from ortho-nitro-phenyl-acetic acid.

This acid can be obtained synthetically from toluene, and it is first converted into the amido-acid, which, like several ortho-compounds, loses water, and is converted into a body called oxindol, from which isatin, and, therefore, indigo, can be obtained. The precise steps to be followed are:

1. Ortho-amido-phenyl-acetic acid yields oxindol:

$$C_6H_4\left\langle\begin{array}{l} CH_2.CO_2H \\ NH_2 \end{array}\right. = C_6H_4\left\langle\begin{array}{c} CH_2 \\ NH \end{array}\right\rangle CO + H_2O.$$

2. This on treatment with nitrous acid yields nitrosoxindol:

$$C_6H_4\left\langle\begin{array}{c} CH(NO) \\ NH \end{array}\right\rangle CO.$$

3. This again, with nascent hydrogen gives amidoxindol:

$$C_6H_4\left\langle\begin{array}{c} CH(NH_2) \\ NH \end{array}\right\rangle CO.$$

4. Which on oxidation gives isatin:

$$C_6H_4\left\langle\begin{array}{c} CO \\ NH \end{array}\right\rangle CO$$

(*Q. E. D.*)

This process, the feasibility of which had also been foreseen by Kekulé, is, however, not available as a practical scheme, for various reasons.

Process No. 3.—This may be called the manufacturing process, and was also proposed by Baeyer. It starts from cinnamic acid, a substance contained in gum benzoin, balsam of Peru, and some few other aromatic bodies. These sources are, however, far too expensive to render this acid, thus obtained, available for manufacturing purposes. But Bertagnini, in 1856, had obtained cinnamic acid artificially from oil of bitter almonds, and other processes for the same purpose have since been carried out. Of these, that most likely to be widely adopted is the following practical modification by Dr. Caro of Mr. Perkin's beautiful synthesis of cinnamic acid:

1. $$\underset{\text{Toluene.}}{C_6H_5CH_3} + 4Cl = \underset{\text{Benzylene dichloride}}{C_6H_5CHCl_2} + 2HCl.$$

2. $$\underset{\text{Benzylene dichloride.}}{C_6H_5CHCl_2} + \underset{\text{Sodium acetate.}}{2CH_3COONa} =$$

$$\underset{\text{Cinnamic acid.}}{C_6H_5CH{=}CH.COOH} + 2NaCl.$$

But why did Baeyer select this 9-carbon acid from which to prepare indigo? For this he had several reasons. In the first place it had long been known that all indigo compounds, when heated with zinc dust, yield indol, C_8H_7N, a body which stands therefore to indigo in the same relation as anthracen to alizarin, and Baeyer and Emmerling had so long ago as 1869 prepared this indol from ortho-nitro-cinnamic acid, thus:

$$C_8H_6(NO_2)CO_2H = C_8H_7N + O_2 + CO_2.$$

Secondly, the ortho-nitro-cinnamic acid required (for we must remember that indigo is an ortho compound and also contains nitrogen) can be readily prepared from cinnamic acid, and this itself again can be obtained on a large scale. Thirdly, this acid readily parts with one atom of carbon, and thus renders possible its conversion into 8-carbon indigo.

The next steps in the process are (3) the formation of ortho-nitro-cinnamic acid; (4) the conversion of this into its dibromide; (5) the separation from this of two molecules of hydrobromic acid, giving rise to ortho-nitro-phenylpropiolic acid, and (6) lastly, the conversion of this latter into indigo by heating its alkaline solution with grape sugar, xanthate of soda, or other reducing agent. These reactions are thus represented:

$$3.\ \underset{\text{Cinnamic acid.}}{C_6H_5CH = CH.COOH} \text{ yields } \underset{\text{Ortho-nitro-cinnamic acid.}}{C_6H_4(NO_2)CH = H.COOH.}$$

In this process the para-acid is also obtained, and, as this is useless for the manufacture of indigo, it has to be removed. This is effected by converting the acids into their ethyl-ethers, which, possessing different degrees of solubility, can be readily separated from one another.

4. This is next converted into the dibromide,

$$C_6H_4(NO_2)CHBr.CHBr.COOH.$$

5. And by careful treatment with caustic soda this yields ortho-nitro-phenylpropiolic acid, thus:

$$\begin{aligned} &C_6H_4(NO_2)CHBr.CHBr.COOH + 2NaOH \\ = &C_6H_4(NO_2)C_2.COOH + 2NaBr + 2H_2O. \end{aligned}$$

$$6.\ n[\underset{\text{Ortho-nitro-propiolic acid.}}{C_6H_4(NO_2)C_2.COOH} + H_2 = \underset{\text{Indigo.}}{C_8H_5NO} + CO_2 + H_2O.$$

(*Q. E. D.*)

The last of these reactions is in reality not so simple as the equation indicates, for only about 40 per cent. of indigo is obtained, whereas, according to theory, 68 per cent. should result. Indeed, although, as we have seen, indigo can be prepared by these three methods, chemists are as yet in doubt as to its molecular weight, the probability being that the molecule of indigo contains twice 16

atoms of carbon, or has the formula $4(C_8H_5NO)$ or $C_{32}H_{20}N_4O_4$. Still, it must be remembered that, according to Sommaruga, the vapor-density of indigo is 9.45—a number corresponding to the simpler formula $C_{16}H_{10}N_2O_2$.

The artificial production of indigo may even now be said to be within reasonable distance of commercial success, for the ortho-nitro-phenyl-propiolic acid—the colorless substance which, on treatment with a reducing agent, yields indigo-blue—is already in the hands of the Manchester calico-printers, and is furnished by the Baden Company for alkali and aniline colors at the price of 6 shillings per lb. for a paste containing 25 per cent. of the dry acid.

With regard to the nature of the competition between the artificial and the natural coloring matters, it is necessary to say a few words. In the first place, the present price at which the manufacturers are able to sell their propiolic acid is 50 shillings per kilo. But 100 parts of this can only yield, according to theory, 68.58 parts of indigo-blue, so that the price of the artificial (being 73 shillings per kilo.) is more than twice that of the pure natural color. Hence, competition with the natural dye-stuff is not to be thought of until the makers can reduce the price of dry propiolic acid to 20 shillings per kilo. and also obtain a theoretical yield from their acid. This may, or it may not, be some day accomplished, but at present it will not pay to produce indigo from nitro-phenyl-propiolic acid. Nevertheless, a large field lies open in the immediate future for turning Baeyer's discovery to practical account. It is well known that a great loss of coloring matter occurs in all the processes now in use for either dyeing or printing with indigo. A large percentage of indigo is lost in the "cold vats" in the sediment. Another portion is washed off and wasted after the numerous dippings, whilst, in order to produce a pattern, much indigo must be destroyed before it has entered into the fibre of the cloth. Moreover, the back of the piece is uselessly loaded with color. In the processes of printing with indigo the losses are as great or even greater, and, in addition, such considerable difficulties are met with that only a few firms (Potter, Grafton in Manchester, and Schliefer in Elberfeld) have been successful in this process. But a still more important fact remains—that no printing process exists in which indigo can be in combination with other colors in the ordinary way, or without requiring some special mode of fixing after printing. Hence, it is clear that the weak points of natural indigo lie in the absence of any good process for utilizing the whole of its coloring matter, and in the impossibility, or, at any rate, great difficulty, of employing it in the ordinary madder styles of calico-printing. Such were the reasons which induced the patentees to believe that, although the artificial dye cannot be made at a price to compete with natural indigo for use in the ordinary dye-beck, it can even now be very largely used for styles to which the ordinary dye-stuff is inapplicable.

To begin with, Baeyer employed (Patent 1177) grape-sugar as a reducing agent. The reduction in this case does not take place in the cold, and even on long standing only small traces of indigo are formed, but if heated to 70° or upwards the change takes place. Unfortunately this production of indigo-blue is rapidly followed by its reduction to indigo-white, and it is somewhat difficult in practice to stop the reaction at the right moment. Bût "necessity is the mother of invention," and Dr. Caro, of Mannheim, to whom the speaker is greatly indebted for much of the above information, found that sodium xanthate is free from many of the objections inherent to the glucose reduction process, inasmuch as the reaction then goes on in the cold. Moreover, he finds that the red isomeride of indigo-blue, Indirubin, which possesses a splendid red color, also occurring in natural indigo, but whose tinctorial power is less than that of the blue, is produced in less quantity in this case than when glucose is employed. On this cloth alumina and iron mordants may be printed, and this afterwards dyed in alizarin, &c., or this coloring matter may also be printed on the cloth and the color fixed by moderate steaming without damage to the indigo-blue. This process is now in actual use by printers both in England and on the Continent, so that, thanks especially to the talent and energy of Dr. Caro, Baeyer's discovery has been practically applied within the short space of twelve months of its conception. Operations on a manufacturing scale have been successfully carried on in the Baden Soda and Aniline Works at Ludwigshofen for the last two months, and the directors see no reason why they should not be able to supply any demand, however great, which may be made for ortho-nitro-phenyl-propiolic acid.

The proper way of looking at this question at present is, therefore, to consider ortho-nitro-phenyl-propiolic acid and indigo as two distinct products not comparable with each other, inasmuch as the one can be put to uses for which the other is unfitted, and there is surely scope enough for both. Still, looking at the improvements which will every day be made in the manufacturing details, he must be a bold man who would assert the impossibility of competing with indigo in all its applications. For we must remember that we are only at the beginning of these researches in the indigo field. Baeyer and other workers will not stay their hands, and possibly other coloring matters of equal intensity and of equal stability to indigo may be obtained from other as yet unknown or unrecognized sources, and it is not improbable that these may turn out to be more formidable competitors in the race with natural indigo than ortho-nitro-phenyl-propiolic acid.

Looking at this question of the possible competition of artificial with the natural indigo from another standpoint of view, it must, on the other hand, be borne in mind that the present mode of manufacturing indigo from the plant is extremely rude and imperfect, and that by an improved and more careful carrying out of the pro-

cess great saving in coloring matter may be effected, so that it may prove possible to produce a purer article at a lower price, and thus to counterbalance the production of the artificial material.

The following are the directions issued by the patentees to calico-printers for using the new color:

Printing with Artificial Indigo.

No. I.—*On Unprepared Cloth.*

Standard.—Take 4 lbs. propiolic acid paste (equal to 1 lb. dry acid) and 1 lb. borax finely powdered; mix well. The mixture first becomes fluid and at last turns stiff. Then add 3 quarts white starch thickening (wheat starch); mix well, and strain.

Printing Color.—Take the above standard and dissolve in it immediately before printing 1½ lbs. xanthate of soda, stir well, and ready for use. For lighter shades reduce the above printing color with the following: In 1 gallon white starch paste dissolve 1 lb. xanthate of soda.

Directions for Use.—Print and dry as usual. The pieces ought not to be placed in immediate contact with drying cylinders, or otherwise subjected to heat above 100° C. The indigo-blue is best developed by allowing the printed goods to remain in a dry atmosphere and at an ordinary temperature for about forty-eight hours. Damp air ought to be excluded as much as possible until the color is fully developed. Then the pieces may be passed through the ageing machine, or steamed at low pressure if such treatment should be required for fixing any other color or mordant printed along with the indigo-blue.

After the blue is ready formed, the pieces are first thoroughly washed in the washing machine and *then boiled* in clean water, or better, in a weak solution of hyposulphite of soda (1 lb. to 10 gallons), *and at a full boil* for half an hour in order to volatilize the smell which would otherwise adhere to the goods.

Clean in a soap-bath, at a temperature not above 40° C.; wash, dry, and finish.

Observations.—Wheat starch gives the best results in the color, then follows gum tragacanth. The color is considerably reduced by using gum senegal, dark British gum, or calcined farina as thickening materials.

So far borax has answered best as an alkaline solvent of propiolic acid; it may, however, be replaced in the above standard by acetate of soda (from 1 to 1½ lbs.) or by 6 ozs. pearl-ash or soda. Any excess of caustic potash, or soda, destroys propiolic acid.

The above standard keeps unchanged for any length of time; it is likewise not sensibly altered by a small amount of xanthate of soda; but when mixed with its full proportion of xanthate, as in the above printing color, it gradually loses strength after several hours.

The xanthate ought, therefore, to be mixed with the standard immediately before printing, and any color remaining unused may then be saved by mixing with the same a large proportion of starch paste.

Propiolic acid may be printed along with aniline-black, catechu brown and drabs, and with alumina and iron mordants for madder colors.

After the indigo-blue is fully developed, the mordants are fixed in the ordinary manner, dyed with alizarin, padded with Turkey-red oil, steamed, and otherwise treated as usual.

Indigo-blue, whether natural or artificial, suffers by prolonged steaming at high pressure. For this reason only such steam colors can be associated with propiolic acid as may be fixed by short steaming at low pressure.

No. II.—*On Prepared Cloths (for Full Shades).*

Dissolve 2 lbs. of xanthate of soda in 1 gallon of cold water. Pad the goods with the above; dry, print with standard, and after printing follow the above treatment. The pieces may also be first printed with xanthate and then covered with standard. Alumina and iron mordants for madder colors may be likewise printed on cloth thus prepared, or printed with xanthate of soda.

The potential importance, from a purely commercial point of view, of the manufacture, may be judged of by reference to the following statistics, showing that the annual value of the world's growth of indigo is no less than four millions (pounds) sterling ($20,000,000).

Estimated Yearly Average of the Production of Indigo in the World, taken from a Total Crop for a Period of Ten Years.

	Pounds weight.	Pounds st'g.
Bengal, Tirhoot, Benares, and N. W. India	8,000,000	2,000,000
Madras and Kurpah	2,200,000	400,000
Manilla, Java, Bombay, etc. . . .		500,000
Central America	2,250,000	600,000
China and elsewhere, consumed in the country,	say	500,000
		4,000,000

How far the artificial will drive out the natural coloring-matter from the market can not, as has been said, be foreseen. It is interesting, as the only instance of the kind on record, to cast a glance at the history of the production of the first of the artificial vegetable coloring-matters, alizarin. In this case the increase in the quantity produced since its discovery in 1869 has been enormous; such indeed that the artificial color has now entirely superseded the natural one, to the almost complete annihilation of the growth of

the madder-root. It appears that while for the ten years immediately preceding 1869 the average value of the annual imports of madder-root was over one million sterling ($5,000,000), the imports of the same material during last year (1880) amounted only to £24,000 ($120,000); the whole difference being made up by the introduction of artificial alizarin. In 1868, no less a quantity than 60,000 tons of madder-root were sent into the market, this containing 600,000 kilos of pure natural alizarin. But in ten years later a quantity of artificial alizarin, more than equal to the above amount, was sent out from the various chemical factories. So that in ten years the artificial production had overtaken the natural growth, and the 300,000 or 400,000 acres of land which had hitherto been used for the growth of madder, can henceforth be better employed in growing corn or other articles of food. According to returns, for which the speaker had to thank Mr. Perkin, the estimated growth of madder in the world previous to 1869 was 90,000 tons, of the average value of £45 ($225) per ton, representing a total of £4,050,000 ($20,000,000).

Last year (1880) the estimated production of the artificial coloring-matter was 14,000 tons, but this contains only 10 per cent. of pure alizarin. Reckoning 1 ton of the artificial coloring-matter as equal to 9 tons of madder, the whole artificial product is equivalent to 126,000 tons of madder. The present value of these 126,000 tons of alizarin paste, at £122 per ton, is £1,568,000. That of 126,000 tons of madder at £45 is £5,670,000, or a saving is effected by the use of alizarin of considerably over four millions sterling. In other words, we get our alizarin dyeing done now for less than one-third of the price which we had to pay to have it done with madder.

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To Englishmen it is a somewhat mortifying reflection, that whilst the raw materials from which all these coal-tar colors are made are produced in our country, the finished and valuable colors are nearly all manufactured in Germany. The crude and inexpensive materials are, therefore, exported by us abroad, to be converted into colors having many hundred times the value, and these expensive colors have again to be bought by English dyers and calico-printers for use in our staple industries. The total annual value of manufactured coal-tar colors amounts to about three and a half millions (pounds sterling); and as England herself, though furnishing all the raw material, makes only a small fraction of this quantity, but uses a large fraction, it is clear that she loses the profit on the manufacture. The causes of this fact, which we must acknowledge, viz., that Germany has driven England out of the field in this important branch of chemical manufacture, are probably various. In the first place, there is no doubt that much of the German success is due to the long-continued attention which their numerous universities have paid to the cultivation of organic

chemistry as a pure science. For this is carried out with a degree of completeness, and to an extent to which we in England are as yet strangers. Secondly, much again is to be attributed to the far more general recognition amongst German than amongst English men of business of the value, from a merely mercantile point of view, of high scientific training. In proof of this it may be mentioned, that each of two of the largest German color works employs no less a number than from twenty-five to thirty highly educated scientific chemists, at salaries varying from £250 to £500 or £600 per annum.

The Chemists at Cincinnati.

On the seventeenth day of August the American Association for the Advancement of Science met at Cincinnati, with President Geo. J. Brush in the chair. The Sub-section of Chemistry was well attended, but the chairman, Professor W. R. Nichols, was absent because of illness. The secretary, Professor Wiley, was also obliged to be absent a large part of the time, and accordingly Prof. G. C. Caldwell and Dr. Albert Springer served as chairman and secretary, respectively. During the meetings the Association adopted a number of amendments to its constitution; one of which elevated the Sub-section of Chemistry to the rank of a full section, and gave to its future chairmen the standing of Vice-Presidents of the whole association. For next year, Prof. H. Carrington Bolton will be the Vice-President over the new section C, and Dr. Springer Secretary.

The day preceding the meeting of the Association, the Society for the Promotion of Agricultural Science met. Before this body, several papers having chemical purport were read. One was by Professor Kedzie, on a vesiculating test for wheat-flour, and another by Professor Caldwell on the analysis of milk.

In the analysis of milk for agricultural purposes, only total dry substance, fat and protein are usually determined. In cases when it is desired to determine the average composition of the milk of a cow, or to test the effect of any special system of feeding on the quality of the milk, or to compare the milk of cows of different breeds, it is not sufficient, as has been shown by Kühn, to analyse the milk of one day, or even of several days distributed at intervals through a certain period; but the milk of every milking of several successive days must be examined.

To avoid the labor of so many separate determinations of dry substance, fat and protein, the writer sets out with a sufficient quantity of properly prepared sand, previously weighed in a weighed porcelain dish, to take up the residue of six or eight milkings: of

the first milking he adds about 10 cc. carefully weighed, and evaporates down to moderate dryness; this residue is set aside till the next milking, when another portion of 10 cc. is added and evaporated in like manner, and so on. Finally the whole is dried down to a point just short of brittleness, when it is carefully pulverized by means of a small pestle made of glass rod; great care is taken as each portion of milk is evaporated to scrape down the residue that adheres to the sides of the dish, with a small spatula made by flattening out the end of a piece of stout platinum wire, and to mix it with the sand. The pulverized residue finally obtained is dried as completely as possible over the water-bath, and then at 100° C. in the drying chamber for an hour, and finally for several days in the desiccator over sulphuric acid. Repeated analyses of a residue obtained and prepared in this manner have shown that it has a uniform composition throughout. It may be sealed up in a flask and kept, if desired, till a more convenient season for determination of fat and protein. The dry residue, fat and protein found give the average composition of the milk for the whole period of three or four days during which the milk was collected.

The writer next spoke briefly of the various methods for the quick determination of the fat for sanitary or technical purposes, and affirmed that all so-called optical methods of testing milk have failed to give satisfaction; that Marchand's lactobutyrometrical method has found increasing favor in the past two years; that Soxhlet's method, depending on the determination with a delicate areometer of the specific gravity of the etherial solution of the fat of the milk, obtained by shaking up definite quantities of the milk and ether together, with the addition of a little potash, gives remarkably accurate results, and promises to be of great utility in the hands of the intelligent dairyman, although the apparatus could not be so well trusted to clumsy hands as the lactobutyrometer. He showed that the formula for calculating the dry substance from the specific gravity and per cent. of fat, given by Behrend and Morgen in Journal für Landwirthschaft **27**, 249, while in most cases yielding very good results, may in some cases give such as are 0.7 per cent. from the correct proportion.

Finally he called attention to the fact that from the results of the very large number of analyses of milk made in Germany in 1879, it appears that milk may fall much below the standard generally accepted as the minimum and still be genuine milk, and gives his approval to the idea that Boards of Health should have the power to pronounce milk to be unfit for sale as good milk when it falls below a certain standard, without any regard to the question whether it was watered or not—that whether watered by giving the cow sloppy fodder, or by adding water to the milk of a properly fed cow, the final result is the same imposition on the public.

On Thursday, the eighteenth, the room of the chemical subsection was given up to the Association of Agricultural Chemists,

before whom a paper by C. M. Stillwell was read, on the "Preparation of samples for analysis." Henceforward this Association will not act as a separate organization, but will be a part of the regular Section of Chemistry.

The active work of the sub-section began on Friday, with a paper by C. W. Dabney, Jr., on "An Isopicraminic Acid." Following this, Professor A. B. Prescott read an essay of H. B. Parsons on "The Composition and Quality of American Wines," and Dr. Springer presented a communication upon "Pentachloramyl formate." A broad glass tube, bent to a quarter circle, was filled with amyl formate, and exposed during five or six days to the combined action of sunlight and a stream of dry chlorine. When the operation was completed the excess of free chlorine and hydrochloric acid were expelled by a current of dry carbon dioxide, and then the product was washed with water and carefully dried. Pentachloramyl formate, thus obtained, is a heavy, colorless liquid of sp. g. 1.52. It fumes considerably when exposed to the air, and has an irritating odor. Cold water does not decompose it in less than three weeks; but water at 70° does. Heated to 108° it becomes brown, and at 120° almost black; hence it cannot be distilled either by itself or with water. It has an acid reaction, and burns with a greenish flame. Exposed to light it undergoes decomposition in about three weeks; but in darkness the time was prolonged to seven weeks. Formula, $C_6H_7Cl_5O_2$. Dr. Springer thinks that in constitution it may be regarded as a chlorocarbonate of tetrachloramyl, from considerations based upon the properties of an ammonia salt derived from it. This salt is still under examination.

The fourth and fifth papers were by Dr. J. Lawrence Smith. First he described and exhibited a specimen of pig iron of uncertain origin, having anomalous chemical properties. It contained sixteen per cent. of silicon, and was absolutely unacted upon by acids. A polished fragment of it which had been long imbedded in iodine showed no signs of rust or corrosion. His other communication was upon the new mineral Hiddenite, of which he exhibited specimens, both uncut and mounted as a gem. Dr. Smith was followed by Miss Virginia K. Bowers, whose paper was entitled: "Is the Law of Repetition the Dynamic Law underlying the Science of Chemistry?" Professor A. B. Prescott next read upon "The limited biological importance of synthetic achievements in organic chemistry."

The solicitude shown for half a century as to the biological bearings of chemical synthesis arises from a misapprehension of the scope of chemical action. It must be accepted, from all we know of the sphere of chemism, (1) that the matter of protoplasm is at all events in a state of chemical combination, but (2) it cannot therefore be accepted that chemical union in itself supplies the essential conditions for organization or other vital functions. This is just the

question of abiogenesis, to be settled by experiment. Chemical action is distinct from organization, as, also, it is from cohesion, adhesion, heat, etc., and its co-relations to all these molecular activities always have to await demonstration.

So far, a cell-growth appears to be indispensable to the simple splitting of sugar into alcohol and carbon dioxide. There may or may not be an essential co-relation between cell-growths and proteid chemical syntheses. The growing vegetable cell may or may not be one of the conditions for the chemical formation of cellulose. The synthesis of the latter certainly can promise nothing of the inception of cell organization.

The closing paper of the day was by R. B. Warder, upon the "Evidence of atomic motion within liquid molecules, as based upon the speed of chemical action."

The experimental evidence upon which the argument of this paper is based has already been published; viz., the author's determinations of the speed of the saponification of acetic ether at different temperatures[1] and Weber's determinations of liquid diffusion.[2] The twenty determinations of speed of saponification just referred to agree pretty closely with an empirical formula of the form

$$a = A + Bt^2$$

where a denotes the "coefficient of speed," and t is the temperature of the mixture.

Weber, on the other hand, shows that the diffusion constant varies nearly according to the linear equation,

$$K = A' + B't.$$

Now when chemical action takes place in a very dilute solution, the solvent will often retard the action for hours or days; the unlike molecules cannot react upon each other unless they are brought very near together; and in what we call a homogeneous fluid this takes place by diffusion. Any change of conditions by which the diffusion is increased may likewise increase the speed of chemical action. But while the increase in the diffusion constant for dilute solutions varies nearly as the *first* power of the temperature, the increase of chemical action (in the case before us) is nearly as the second power of the temperature. From these facts I conclude that the increase in the rate of diffusion alone is not sufficient to account for the increased rate of chemical action, and a second cause for the increased speed of the reaction must be sought in the atomic motion within the liquid molecules. If the amplitude of the atomic vibrations is increased by raising the temperature (no matter what the nature of those vibrations may be), we must suppose that they recede further from the conditions of mean equilibrium,

[1] Ber. d. c. G. **14**, 1361. [2] Wied. Annal. **7**.

the stability of the molecule would most probably be diminished thereby, and the frequency of a metathesis would accordingly be increased, as shown by the determinations already referred to.

On Saturday, the following papers were read: "The Constitution of the Atom of Science," by Mrs. A. B. Blackwell. "An attachment for burettes avoiding the necessity of using glass stopcocks," by Professor F. A. Roeder. Professor Roeder also exhibited and described an interesting new form of analytical balance. Both of these communications were valuable, but neither could be made clear to readers without the use of diagrams. "Amylose; its nature and methods of analysis," by Professor H. W. Wiley. Later in the day the same chemist read upon the "Relation of reducing power as measured by Fehling's solution to the rotatory power of glucose and grape sugar." Dr. J. Lawrence Smith described a regulator for filter pumps, and Professor W. O. Atwater presented a communication on "The sources of the nitrogen of plants."

This paper gave the results of a series of experiments with plants grown in sand, to which known quantities of plant-food were supplied. The amount of nitrogen at the end of the experiment, *i. e.* in the plant and soil together, was greater than that supplied in seed and nutritive solution. The excess, which was equal to about one-fourth of the whole nitrogen of the plants, must have come from the air. The experiments do not prove, however, that this nitrogen was taken from the air by the foliage of the plants, though it is not easy to see how so large a quantity could have been absorbed by the nutritive solution and thus communicated to the plants through the roots. The experiments are being repeated with appliances for studying this latter question.

On Monday, August 22, the Sub-section of Chemistry finished up its work and adjourned. First, Professor Wiley read a paper upon "Mixed or New Process Sugars, with Methods and Results of Analyses." He was followed by Professor Henry Carmichael, with two communications—one on a "Filtration Evaporation Balance," and the other upon "The Liquefaction of Glass in Contact with Water at 250°C." Professor Wiley then described "A New Material suitable for Stop-Cocks and Stoppers for Reagent Bottles." This was the so-called "Mayall metal," made by T. J. Mayall, of Reading, Mass., which consists of 5 to 6 parts graphite, 1 part rubber and ½ part sulphur. Instead of sulphur, sulphide and antimony may be used. Next came papers by Professor W. O. Atwater, in abstract as follows:

The Chemistry of Fish and Invertebrates.—This paper gave a report of progress during the past year of an investigation which is being conducted under the auspices of the Smithsonian Institution and the U. S. Fish Commission, in the chemical laboratory of Wesleyan University, and of which an account was given at the Boston meeting of the Association.

The number of samples thus far analyzed is seventy-six, of which fifty-one are fish and twenty-five invertebrates, oysters, lobsters, etc. The investigation is to be reported in detail in the Report of the U. S. Fish Commission, and perhaps elsewhere.

The Quantitative Estimation of Chlorine.—The applicability of Volhard's method for the determination of chlorine in organic (animal and vegetable) compounds was tested by trials with known amounts of sodium chloride mixed with sugar, the mixture being fused with sodium carbonate and nitrate, the fusion dissolved in nitric acid, silver nitrate added in excess, and the latter determined with sulphocyanide solution by the method of Volhard. It appears that especial care is needed in the fusion; but, if this be conducted slowly and at a low temperature, there is no appreciable loss of chlorine. This done, the precautions mentioned by Volhard will, with proper manipulation, insure very accurate results. Direct determination of chlorine in the fusion by precipitation and weighing as silver chloride, as has been recommended, brings results far too low, on account of the solubility of silver chloride in sodium nitrate. The determination by Volhard's method is convenient and satisfactory.

Last of all came a communication by Professor G. C. Caldwell, on "Some New Forms of Laboratory Apparatus."

For a water-bath heated by steam the writer uses a strong cast iron box, about 5 inches deep and 6 inches broad and from 2 to 3 feet long, according to the number of water-baths to be heated, into which steam from the boiler is conducted, while the waste and condensed water is allowed to flow out through a narrow opening, regulated by a stop-cock in the bottom at the other end. Cup-like depressions 3 or 4 inches in diameter and 3 inches deep are sunk in this box from the upper surface, which communicate with a supply of water through pipes passing from the bottom of each cup and through the bottom of the box to a small main running along beneath the box; water slowly flowing through these cups, and through an outlet beyond them which is raised about as high as the middle of the cups, is easily kept constantly boiling by the steam circulating within the space around the cups.

For the determination of the specific gravity of liquids the writer fills a weighed pipette provided with a short and fine beak and an upper tube with very fine bore, with a volume of liquid occupying the space between the point below and a mark on the tube above; with the aid of a properly constructed clamp, for the detailed description of which we have no room, the pipette is easily and very accurately filled with a constant volume of any liquid at any ordinary temperature.

For hot filtration with the Bunsen pump, a funnel with a long neck is put first through a cork in the neck of a small bottle, about two-thirds of whose body has been cut off, in such a manner that the part of the bottle left surrounds the funnel nearly to its top;

the beak of the funnel is next passed through a cork in the tubulure of a bell jar; a short glass tube also passed through the same cork provides for connecting the interior of the bell jar with the pump. The space around the funnel is partly filled with water, a glass tube is carried from a flask to the bottom of this space where it ends in a fine jet; the bell jar is set on a ground-glass plate on which a beaker is placed to receive the filtrate, connection is made with the pump, water is boiled in the flask, and the steam driven over to the water around the funnel soon heats that to boiling, and the contents of the funnel are kept hot during the filtration; the water that accumulates around the funnel is quickly returned to the flask by removing the lamp for a moment.

For the student's Gooch's crucible, in short courses of quantitative analysis, when the purchase of a platinum crucible can hardly be afforded, the writer proposes to use a porcelain crucible made with only a narrow ledge around the bottom; on this ledge a perforated disk of thick platinum foil can be placed, and the asbestos will easily close all the interstices between the foil and the ledge on which it rests. Such crucibles can be furnished by German manufacturers at the same rates as ordinary crucibles of the same size.

The next meeting of the Association, under the presidency of J. W. Dunson, will be held in Montreal, beginning on the last Wednesday of August, 1882.

F. W. Clarke.

A Manual of Sugar Analysis, including the application in general of analytical methods to the sugar industry, with an introduction of the chemistry of cane-sugar, dextrose, levulose, and milk-sugar. By J. H. Tucker, Ph. D. New York: D. Van Nostrand, 23 Murray Street, and 27 Warren Street.

The object of this book is to present, in easily accessible form, to the public directly or indirectly connected with the sugar interests of this country, the results of investigations on sugar analysis, collected from German, English and French writers. The book is a valuable one for students in chemistry taking special interest in the analysis of sugars, inasmuch as it gives all technical analytical methods in use at the present time in sugar factories and commercial laboratories.

The physical and chemical methods for determining various kinds of sugars are given complete, as are also the methods for the analysis of bone-black, a product so extensively used for its absorptive power for coloring matter, organic and inorganic salts, etc., in the course of the manufacture of different sugars.

The chemistry of sugar is treated in chapters I, II, III, and IV, which contain the literature of cane-sugar, dextrose, levulose, and milk-sugar, up to the present time, in a condensed form.

It is, however, to be regretted that Mr. Tucker, in speaking of the melassigenic action of salts upon solutions of cane-sugar, omitted mentioning the method of Scheibler, by which almost all saccharose (cane-sugar) can be separated from salts and organic nitrogenous substances that are met with in ordinary beet-root molasses. This method is extensively used in Europe, and consists in the separation of the saccharose as calcium sucrate. The salts and nitrogenous organic substances that remain unacted upon in the treatment of molasses with caustic lime are dissolved by alcohol of a specific strength.

Although caustic lime is mentioned as influencing the rotatory power of cane-sugar, it is not stated how calcium sucrate and other sucrates have to be treated in order to obtain correct results with the polariscope.

Chapter X, on the analysis of molasses and syrups, is not as exhaustively treated as one would expect, considering the number of publications on the subject, the methods in use for determining nitrogen, carbon, hydrogen and oxygen being entirely omitted. It would have added to the value of the book if it had been stated how the above-named elements, particularly nitrogen, are quantitatively and qualitatively determined and detected in sugar-house molasses and syrups; it being known that nitrogen is playing an important part in Vincent's process for manufacturing on a large scale trimethylamine in connection with the distillation of alcohol from fermented beet-root molasses. In most respects, however, the book can be cordially recommended.

C. Fahlberg.

Philadelphia, *October 5th*, 1881.

NOTES.

Colliery Explosions.

F. A. Abel has experimented upon several samples of coal dust obtained from the Seaham Colliery after the explosion of September, 1880.

Some of the samples appeared to have been affected by heat; but the chemical and microscopical examinations did not indicate the part taken by the coal dust in producing and transmitting the explosion. With a view to ascertaining the influence which coal dust exerts upon explosions in mines, the apparatus devised by

Galloway was employed, with some modifications. Samples of the Seaham dust which contained the largest proportion of coal were the most sensitive in producing the ignition of fire-damp. Explosions were effected with them in air containing only 2.5 per cent. of fire-damp. One sample of dust which was third in order of sensitiveness contained the lowest proportion of coal of all the others. Experiments were accordingly undertaken which showed that perfectly non-combustible powders (*e. g.* calcined magnesia) are, when exposed to the heat of a flame, nearly as effective as the highly sensitive dusts in producing ignition of air and fire-damp, which may otherwise constitute a non-explosive mixture. A mixture of fire-damp and air, containing 2.75 per cent. of the former gas, was allowed to pass a flame for some time at a velocity of 600 feet per minute. No explosive effect was produced, but, when the mixture was caused to convey calcined magnesia, a feeble explosion resulted.

The conclusions reached from the experiments with the dusts from the Seaham and other mines are:

(*a*) "That coal dust in mines not only much promotes and extends explosions in mines by reason of the rapid inflammability of the finely-divided combustible, and of the readiness with which it becomes and remains suspended in air-currents"; but

(*b*) "That it may also be itself brought into operation as a fiercely-burning agent which will carry flame rapidly as far as its mixture with air extends, and will operate even as an exploding agent through the medium of a proportion of fire-damp in the air of the mine, the existence of which, in the absence of the dust, would not be attended by any danger."

(*c*) "That dust in coal mines, quite apart from any inflammability which it may possess, can operate in a distinct manner as a finely-divided solid in determining the ignition of mixtures of only small proportions of fire-damp and air, and consequently in developing explosive effects."

It also appears that the proportion of fire-damp which is necessary to cause an explosion is below that which can be detected by the most experienced observers.—(*Chemical News*, **44**, 16, 27, 39.)

C. P.

Constitution of Phosphonium and Arsenium Compounds.

V. Meyer and M. Lécco[1] observed that the compound of dimethyl-ethyl-amine with ethyl chloride is identical with the compound formed by the union of methyl chloride with diethyl-methyl-amine. This compound is thus shown to be atomic and the nitrogen contained in it quinquivalent.

A. Michaelis and A. Link, following the same train of thought, have extended their observations to similar compounds of phosphorus and arsenic.

[1] Ber. deutsch. chem. Gesel. **10**, 233.

The bases

$$(C_6H_5)_2PCH_3 \qquad (C_6H_5)_2AsCH_3$$
$$(C_6H_5)_2PC_2H_5 \qquad (C_6H_5)_2AsC_2H_5$$

were caused to unite with ethyl iodide or methyl iodide with the formation of the compounds,

$$(C_6H_5)_2PCH_3.C_2H_5I \qquad (C_6H_5)_2AsCH_3.C_2H_5I$$
$$(C_6H_5)_2PC_2H_5.CH_3I \qquad (C_6H_5)_2AsC_2H_5.CH_3I$$

Isomerism of the products would imply the trivalence of these elements, identity on the other hand would indicate that they are quinquivalent. Perfect identity of these iodides was observed, thus showing that phosphorus and arsenic are probably quinquivalent. (*Annalen der Chemie*, **207**, 193.)

Free Fluorine.

The nature of the substance with a strong odor which occurs in the colored variety of fluor-spar from Wölsendorf has frequently been the subject of discussion, but up to the present no satisfactory conclusion has been reached. Oscar Loew has recently suggested that the substance may be free fluorine. He has also performed some experiments with the view of testing the correctness of the suggestion. It has been shown by Schrötter that the odor is not destroyed at 310°; that the odor is markedly changed by rubbing the mineral with caustic potash; that rubbed with sulphur an odor of sulphur chloride is produced; and that, further, the substance in question sets chlorine free from sodium chloride and iodine from potassium iodide. To these observations Loew adds that, when the mineral is triturated with dilute caustic potash, a solution is obtained which instantaneously decolorizes a solution of indigo, just as a hypochlorite would do.

One kilogram of the mineral was triturated with ammoniacal water as long as the liquid showed an alkaline reaction. The filtrate was treated with sodium carbonate, evaporated, the residue together with concentrated sulphuric acid brought into a platinum vessel and this covered with glass. The apparatus was allowed to stand for some time at a temperature of 40–50°. The result was a very marked etching of the glass. This experiment is regarded by Loew as proving the correctness of his view.

As cerium occurs in the fluor-spar from Wölsendorf, the hypothesis is put forward that the free fluorine is a result of the dissociation of cerium fluoride, the latter substance having, in all probability, originally been deposited with the calcium fluoride.—(*Ber. deutsch. chem. Gesell.* **14**, 1144.)

On the Occurrence of Free Fluorine.

As regards the possible formation of fluorine from cerium fluoride (see preceding note) K. BRAUNER calls attention to the fact that we know nothing about the properties of cerium tetrafluoride, the compound which Loew had in mind, nor do we even know that it exists. Further, it is known that most varieties of fluor-spar lose their color when heated, and, as the Wölsendorf mineral is strongly colored, it is probable that it has never been heated to a high temperature. Brauner has for some time been engaged in the study of the fluorides which correspond to the peroxides. Two of these are of importance for this discussion, viz. cerium tetrafluoride, $CeF_4 + H_2O$, and its double salt, $3KF.2CeF_4 + 2H_2O$. When the former salt is heated to dark red, the lower fluoride is left:

$$CeF_4.H_2O = CeF_3 + H_2O + F, \text{ or}$$
$$2(CeF_4.H_2O) = 2CeF_3 + 2HF + O + H_2O.$$

If the tetrafluoride is heated at first gently to drive off the water, and afterwards in a covered crucible to a somewhat higher temperature, the gas in the crucible has a very characteristic odor, quite different from that of hydrofluoric acid. The odor is so very like that of chlorine and hypochlorous acid, that some chemists who witnessed the experiment and had knowledge of the nature of the gas were firmly of the opinion that it was chlorine.—(*Ber. deutsch. chem. Gesell.* **14**, 1944.)

On the Petroleum from the Caucasus.

In a former communication attention was called to the researches of BEILSTEIN and KURBATOW on the petroleum obtained from Baiku on the Caspian sea. The oil was found to differ from the American in containing addition products of the aromatic hydrocarbons of the general formula C_nH_{2n}, examples of which are hexahydrobenzene, C_6H_{12}, hexahydrotoluene, C_7H_{14}, etc. The same chemists have now examined the petroleum from the wells belonging to the firm of Siemens and Halske, at Zarskije Kolodzy in the centre of the Caucasus. They separated the oil into three portions boiling respectively at 30–35°, 70–75° and 95–100°. The first fraction consists of pentane, the second of hexane and the third of heptane. The presence of benzene and toluene was also proved. Hence it is seen that the petroleum from the central Caucasus has a different composition from that obtained from the neighborhood of the Caspian sea. It consists essentially of the hydrocarbons C_nH_{2n} which also occur in American petroleum, and contains in addition small quantities of the aromatic hydrocarbons C_nH_{2n-6} (which have also been detected in Hannoverian petroleum) and of the hydrocarbons C_nH_{2n} first found in the petroleum from Baiku.—(*Ber. deutsch. chem. Gesell.* **14**, 1620.)

Commercial Petroleums.

OGLOBLINE has been engaged in an examination of petroleum from different sources, and his results are summed up thus. Although the specific gravity of the American petroleum is less than that of the Caucasian, the former contains a greater proportion of heavy oils. Both varieties emit inflammable vapor at so low a temperature that their use in the crude state is attended with danger. The Caucasian oil is not more difficult to purify than the American, and it is superior to the latter as an illuminating agent. As far as expense and intensity of light are concerned, the Caucasian oil burns better with a flat wick, the American oil with a round wick; the height of the end of the wick above the surface of the oil has a much greater effect on the illuminating power of the latter than on that of the former.—(*Bull. Soc. chimique*, [2], **34**, 682.)

Artificial Production of Crystallized Quartz.

Crystallized quartz has several times been prepared artificially: first by Sénarmont, who obtained it by heating gelatinous silica with hydrochloric acid; then by Daubrée, by the action of superheated water on glass; and lastly, by Hautefeuille, who treated silica at 750–800° with sodium tungstate. C. FREIDEL and E. SARASIN have now prepared it by heating to a temperature below dull redness in a closed steel tube lined with copper, a mixture of potash, alumina, and gelatinous silica, the last in excess, in presence of water. In this way, after continuing the heat, in one experiment for 14 and in another for 38 hours, they obtained silica wholly or almost wholly crystallized.

The first experiment yielded numerous very regularly formed crystals of the ordinary quartz form (prism with the two rhombohedrons), which acted strongly on polarized light in the manner of native quartz. In the second experiment the crystals were larger (up to 0.5 mm. long, and 0.1 mm. broad), but mostly broken off at one end. They sometimes had the form of more acute rhombohedrons, with indications of tetartohedral forms, and many of them exhibited striations and modes of aggregation well known in native quartz.—(H. W. in *Journal Chem. Soc.* from *Jahrbuch für Mineralogie*, 1880, **1**, 179.)

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IX.—ON THE DIASTATIC ACTION OF SALIVA.

By R. H. Chittenden and W. L. Griswold.

I.—*Influence of Acids, Alkalies, and Gastric Juice on the diastatic Action of Saliva.*

Human mixed saliva ordinarily possesses, when freshly secreted, an alkaline reaction. The saliva of the parotid gland, however, which contains the greater part of the diastatic ferment, has, according to Astaschewsky,[1] a very faint acid reaction, which gives place to an alkaline reaction when the mucous membrane of the mouth is strongly irritated. According to the same investigator, the maximum of the diastatic action of parotid saliva corresponds with the strongest acid reaction. It has usually been stated that a slight alteration of the reaction of saliva does not affect its diastatic action; thus years ago Jacubowitsch and Paschutin reported that the addition of caustic soda to distinct alkaline reaction did not hinder the action of the ferment, while, according to Schiff, the ferment was irredeemably destroyed by acids. On the other hand, Lehman,[2] Schiff, Ebstein and others agreed that the addition of small quanti-

[1] Centralblatt f. d. med. Wissensch. 1878, 15.

[2] See Maly in Hermann's Handbuch der Physiologie, Band 5, Theil 1, p. 33.

ties of acids was without influence on the conversion of starch into sugar. Again Jacubowitsch[1] reported the results of several experiments where the gastric juice of a dog was mixed with human saliva in such proportions that neutral, acid and alkaline solutions were obtained, and in all of these cases the action upon starch was the same; all three fluids furnished sugar, but in these experiments there was nothing to indicate the amounts of sugar formed. Watson[2] found as a result of experiment that by the addition of small quantities of acid the diastatic action of saliva was decidedly increased; thus he found that while 400 grains of plain saliva yielded 1.234 grains of glucose, the same amount of saliva, acidified by the addition of one drop of hydrochloric acid (sp. gr. 1.16), yielded 1.708 grains of glucose. From this he concludes that "saliva will be more active upon farinaceous bodies when mixed with the acid fluid of the stomach than it would otherwise be." Munk[3] found that diastase from saliva and pancreatic juice was hindered in its action by .2 per cent. hydrochloric acid, but would tolerate a relatively higher grade of alkalescence.

Naturally in experiments of this kind the concentration of the fluid has considerable influence on the action of the ferment. Thus Paschutin[4] remarks that if carefully neutralized saliva is diluted with water in various proportions, it will be found that a content of acid which, in the undiluted saliva, would cause a greater or less diminution of the diastatic action, will in more dilute samples actually aid in the diastatic process. That the ferment is not destroyed is manifested by the fact that after neutralization of the acid the action again goes on. Thus Maly,[5] basing his observations on these data, says the conversion of starch in the stomach will continue or not according to the quantity of the acid present and its proportion to the ferment present. Therefore, says Maly, the percentage of acid which absolutely hinders can be designated only for a definite mixture and not in a general sense. So Brücke[6] found, when he added to neutralized saliva an equal volume of very dilute hydrochloric acid (.2 per cent.), that the mixture no longer possessed the property of converting starch into sugar. If the mixture contained but one-half gram of hydrochloric acid or

[1] See Lehman's Zoochemie, p. 22. [2] Jour. Chem. Soc. 1879, 543.

[3] See abstract in Jahresbericht u. d. Fortschritte d. Thierchemie für 1876, 271.

[4] Archiv. f. Anat. u. Physiol. 1871, 305.

[5] Hermann's Handbuch d. Physiologie, 5 B. 1 Theil, 34.

[6] Sitzungsber. d. Wiener. Acad. 3 Abth. 1872.

less to the litre, the fluid then was capable of changing the starch into sugar. Hammastern[1] likewise found that in the majority of cases a content of .05–.25 per cent. of hydrochloric acid entirely stopped the diastatic action.

It is thus very evident that there is a great diversity of opinion in regard to the influence of acids and alkalies on the diastatic action of saliva, and likewise as to the effect of acid of the strength of the gastric juice when the two fluids are mixed in the stomach during normal digestion. It is quite natural that the diastatic action of saliva should vary somewhat at different times and under different circumstances; thus variations of temperature, concentration of fluid, length of time of digestion, etc., probably exert some modifying influence, particularly as recent investigation has shown the presence of several carbohydrate products as a result of salivary digestion. Therefore the different experiments about to be described were carried on in series and in such a manner as to obtain uniformity in the various steps of the process, while at the same time one experiment of each series serves as a control, by means of which the diastatic action of the acid or alkaline saliva can be compared with the diastatic action of normal saliva of the same collecting, thus enabling us to accurately measure the influence of the acid or alkali on the diastatic action.

Again it is an important point to ascertain, if possible, the effect of the acid and alkaline fluids of the stomach and intestines on the action of saliva, and as the acid gastric juice is present in the stomach during digestion in great excess over the saliva, we deemed it more in accord with the conditions as they exist in the body to have the saliva present in these experiments in the proportion of one-fourth of the whole mixture. Thus in each digestion 100 cc. of fluid were used, of which 25 cc. were filtered mixed saliva.

The method employed in conducting the digestions was as follows: 1 gram of starch was made into a paste by boiling with 25 cc. of water, then, when cold, 50 cc. of the diluted acid or alkali were added, and finally 25 cc. of filtered human saliva; while, in the control experiment, 50 cc. of water were added in place of the acid or alkali, so that the dilution was the same in each case. The mixtures were then placed in a water-bath at 38-40°C. for a definite period, usually 45 minutes, with occasional stirring. At the end of

[1] Jahresber. d. ges. Med. 1871, 1.

this time the fluid was carefully neutralized and then quickly boiled to destroy the ferment. The mixture was then diluted with water to 500 cc., and, when thoroughly mixed, 50 cc. of this fluid were filtered from the unchanged starch, and in this one-tenth the sugar and other reducing substances were determined gravimetrically according to the method which has been so carefully elaborated by Maercker[1] and others.

The Fehling's solution was prepared by dissolving 34.632 grams of pure cupric sulphate in 1 litre of water. A second solution was made by dissolving 63 grams of sodium hydroxide and 173 grams of recrystallized potassium and sodium tartrate likewise in 1 litre of water. When the sugar was to be determined, 25 cc. of each solution were placed in a small beaker, and then 50 cc. of the diluted and filtered digestive mixture were added, making thereby 100 cc. of fluid. The beaker was then placed in a bath of boiling water for 20 minutes, after which the precipitate of cuprous oxide was filtered off and washed with 300 cc. of boiling water. After drying, the precipitate was ignited in a current of hydrogen and weighed as metallic copper, from which the amount of reducing substance, calculated as dextrose, was ascertained by the use of the tables devised by Maercker, who determined by means of pure dextrose the reduction equivalent of different quantities of sugar under the conditions above described.

First Series of Experiments.[2]

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0864 gram Cu. Entire yield of dextrose, .4685 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .09305 gram Cu. Entire yield of dextrose, .5155 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0797 gram Cu. Entire yield of dextrose, .422 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0081 gram Cu. Entire yield of dextrose, .0429 gram.

[1] Die Landwirthschaftliche Versuchs-Stationen, 25, 115-116.

[2] The saliva used in each series of experiments was collected at one time, thoroughly mixed, and then filtered.

SECOND SERIES OF EXPERIMENTS.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0892 gram Cu. Entire yield of dextrose, .4835 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .1054 gram Cu. Entire yield of dextrose, .5357 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0477 gram Cu. Entire yield of dextrose, .2655 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .01135 gram Cu. Entire yield of dextrose, .0578 gram.

THIRD SERIES OF EXPERIMENTS.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0898 gram Cu. Entire yield of dextrose, .487 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0926 gram Cu. Entire yield of dextrose, .5085 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0671 gram Cu. Entire yield of dextrose, .3455 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .007 gram Cu. Entire yield of dextrose, .036 gram.

FOURTH SERIES OF EXPERIMENTS.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0833 gram Cu. Entire yield of dextrose, .4465 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0921 gram Cu. Entire yield of dextrose, .506 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .05 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0761 gram Cu. Entire yield of dextrose, .399 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0735 gram Cu. Entire yield of dextrose, .3815 gram.

V. 1 gram starch in 25 cc. H_2O+50 cc. .3 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0791 gram Cu. Entire yield of dextrose, .419 gram.

Fifth Series of Experiments.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0873 gram Cu. Entire yield of dextrose, .4735 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .01 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .083 gram Cu. Entire yield of dextrose, .4445 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .05 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0789 gram Cu. Entire yield of dextrose, .418 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0742 gram Cu. Entire yield of dextrose, .3853 gram.

V. 1 gram starch in 25 cc. H_2O+50 cc. .3 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0602 gram Cu. Entire yield of dextrose, .3065 gram.

Sixth Series of Experiments.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0808 gram Cu. Entire yield of dextrose, .428 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .05 per cent. $HCl+25$ cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0742 gram Cu. Entire yield of dextrose, .3855 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. $HCl+25$ cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced an unweighable trace of Cu.

IV. 1 gram starch in 25 cc. H_2O+50 cc. of an active gastric juice[1] containing .05 per cent. $HCl+25$ cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0991 gram Cu. Entire yield of dextrose, .5615 gram.

V. 1 gram starch in 25 cc. H_2O+50 cc. of an active gastric juice containing .1 per cent. $HCl+25$ cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. failed to show any reducing power whatever.

Seventh Series of Experiments.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 65 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .079 gram Cu. Entire yield of dextrose, .4185 gram.

II. 25 cc. saliva + 50 cc. .2 per cent. HCl. Warmed at 38–40°C. for 2 hours; solution then neutralized, 1 gram starch in 25 cc. H_2O added to the neutralized fluid, and the mixture warmed at 38–40°C. for 45 min., boiled and

[1] The gastric juice used in the different experiments was prepared by adding to 100 cc. hydrochloric acid of the strength specified, 5 cc. of a glycerin extract of pepsin, made from the cardiac mucosa of a pig's stomach.

diluted to 500 cc., 50 cc. sol. reduced .0219 gram Cu. Entire yield of dextrose, .1112 gram.

III. 25 cc. saliva + 50 cc. of an active gastric juice containing .2 per cent. HCl. Warmed at 38–40°C. for two hours; solution neutralized, 1 gram starch in 25 cc. H_2O added, and the mixture kept at 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. gave only a very slight trace of Cu_2O.

Eighth Series of Experiments.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0982 gram Cu. Entire yield of dextrose, .5565 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0048 gram Cu. Entire yield of dextrose, .0244 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .01 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0965 gram Cu. Entire yield of dextrose, .545 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. .6 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0808 gram Cu. Entire yield of dextrose, .428 gram.

V. 1 gram starch in 25 cc. H_2O+50 cc. gastric juice containing .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced only a very slight trace of Cu.

VI. 25 cc. saliva + 50 cc. .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. H_2O added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0361 gram Cu. Entire yield of dextrose, .1982 gram.

VII. 25 cc. saliva + 50 cc. gastric juice containing .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. H_2O added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. yielded only a very slight trace of Cu_2O.

Ninth Series of Experiments.

I. 1 gram starch in 25 cc. H_2O+50 cc. H_2O+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0776 gram Cu. Entire yield of dextrose, .407 gram.

II. 1 gram starch in 25 cc. H_2O+50 cc. .1 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0762 gram Cu. Entire yield of dextrose, .3995 gram.

III. 1 gram starch in 25 cc. H_2O+50 cc. .6 per cent. Na_2CO_3+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0765 gram Cu. Entire yield of dextrose, .401 gram.

IV. 1 gram starch in 25 cc. H_2O+50 cc. gastric juice containing .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0981 gram Cu. Entire yield of dextrose, .556 gram.

V. 25 cc. saliva + 50 cc. .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. H_2O added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0129 gram Cu. Entire yield of dextrose, .066 gram.

VI. 25 cc. saliva + 50 cc. gastric juice containing .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. H_2O added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. showed no trace of sugar.

Arranging these results in tabular form we have Table I., in which the figures represent the entire amount of dextrose expressed in grams obtained from one gram of starch by the action of 25 cc. of saliva. The percentages represent the amount of acid or alkali in the entire fluid, viz. in the 100 cc.

TABLE I.

	1st Series.	2d Series.	3d Series.	4th Series.	5th Series.	6th Series.	7th Series.	8th Series.	9th Series.
H_2O	.4685	.4835	.4870	.4465	.4735	.4280	.4185	.5565	.4070
.005 per cent. HCl	.5155	.5357	.5085	.5060	..	..	..	..	..
.025 per cent. HCl	.4220	.2655	.3455	..	..	.3855	..	..	..
.050 per cent. HCl	.0429	.0578	.0360	..	..	0	..	.0244	..
.005 per cent. Na_2CO_3	..	..	..	..	.4445	..	..	.5450	..
.025 per cent. Na_2CO_3	..	..	..	.3990	.4180	..	..	..	..
.050 per cent. Na_2CO_3	..	..	..	.3815	.3853	..	..	..	.3995
.150 per cent. Na_2CO_3	..	..	..	.4190	.3065	..	..	..	..
.300 per cent. Na_2CO_3	..	..	..	..	..	..	..	.4280	.4010
.025 per cent. HCl gastric juice	..	..	..	..	..	.5615	..	..	.5560
.050 per cent. HCl gastric juice	..	..	..	..	..	0	..	0	..
Saliva warmed with .2 per cent. HCl for 2 hours, then neutralized and used	..	..	..	..	..	..	.1112	.1982	.0660
Saliva digested with .2 per cent. HCl gastric juice for 2 hours, then neutralized and used	..	..	..	..	..	.	0	0	0

In order to have the rate of increase or decrease in the diastatic action of the saliva more apparent under the various conditions, Table II. has been devised, showing the ratio of each determination to its control, making the latter 100.

TABLE II.

	1st Series	2d Series	3d Series	4th Series	5th Series	6th Series	7th Series	8th Series	9th Series	Mean Ratio
H_2O	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.
.005 per cent. HCl	110.02	110.79	104.41	113.32	..	..	..	..	..	109.63
.025 per cent. HCl	90.07	54.91	70.94	..	..	90.07	..	..	..	76.49
.050 per cent. HCl	9.15	11.95	7.39	..	..	0	..	4.38	..	8.21
.005 per cent. Na_2CO_3	..	..	..	..	93.87	..	..	97.93	..	95.90
.025 per cent. Na_2CO_3	..	..	..	89.36	88.27	..	..	..	..	88.81
.050 per cent. Na_2CO_3	..	..	..	85.44	81.37	..	..	..	98.15	88.32
.150 per cent. Na_2CO_3	..	..	..	93.84	64.73	..	..	..	..	79.28
.300 per cent. Na_2CO_3	..	..	..	..	..	..	..	76.90	98.52	87.71
.025 per cent. HCl gastric juice	..	..	..	..	..	131.19	..	..	136.60	133.89
.050 per cent. HCl gastric juice	..	..	..	..	..	0	..	0	..	0
Saliva warmed with .2 per cent. HCl for 2 hours, then neutralized and used	..	..	..	..	..	..	26.57	35.61	16.21	26.13
Saliva digested with .2 per cent. HCl gastric juice for 2 hours, then neutralized and used	..	..	..	..	..	..	0	0	0	0

By a glance at the above results we notice first that the presence of acid to the extent of .005 per cent. decidedly increases the diastatic action, while an increase of acid beyond this percentage diminishes the diastatic action of the saliva to a very marked degree. Further experiments conducted with still stronger solutions of acid (.1 per cent., .2 per cent. and .4 per cent. HCl), showed the action to be wholly stopped. The increase in the amount of sugar formed in a faintly acid solution (.005 per cent.) would tend to corroborate the statement of Astaschewsky[1] that the maximum of the diastatic action of parotid saliva corresponds with the strongest acid reaction. The next most noticeable feature is the effect produced by the addition of sodium carbonate, the diastatic action being somewhat diminished, though not materially further affected by an increased percentage of the alkali. The fluids of the intestinal canal are distinctly alkaline, the pancreatic juice, which is most actively concerned in the chemical changes occurring in the intestines, is likewise strongly alkaline; containing presumably an amount of alkali corresponding to .3 per cent. of sodium carbonate. The above experiments then show that an alkaline solution of the strength most favorable for the digestive action of trypsin does not impede to any great extent the action of the ptyalin of pancreatic juice, while any salivary ptyalin which may have survived the action of the gastric juice would again be active

[1] Centralblatt f. d. med. Wissensch. 1878, 15.

under the conditions of the intestinal canal. Just here it may be well to notice the probable effect of a mixture of saliva and gastric juice. Most authorities agree in the statement that the action of saliva is arrested in the stomach by the acidity of the gastric juice, but that when the acid of the chyme is neutralized by the fluids of the intestinal canal the diastatic action of the saliva again goes on. Watson, however, as already quoted, states that saliva will be more active on starchy matters when mixed with the acid fluid of the stomach than it would otherwise be. Our experiments show conclusively that long before the strength of acid approximates to the acid of gastric juice, the diastatic action of the saliva is entirely stopped. Again Maly[1] says that "the salivary ferment is not altered or digested in the stomach, for Connheim found that after 24 hours digestion in an active gastric juice, its diastatic action was again apparent on neutralization."

Our experiments, however, would seem to indicate the incorrectness of the above statement. The experiments, as the preceding results show, were first tried by mixing together gastric juice, starch and saliva, and warming this mixture at the body temperature. When the percentage of hydrochloric acid was .025 there was a notable increase in the diastatic action, for which it is hard to find a suitable explanation. The gastric juice itself, however, appeared to possess to a very slight degree the power of converting starch into sugar, probably in virtue of the presence of a trace of the pyloric ferment in the glycerin, but experiment showed that this could not have played a very important part in the increased formation of sugar.[2] With .05 per cent. hydrochloric acid gastric juice the action was wholly stopped. By previously digesting saliva with an active gastric juice for two hours at 40° C. the diastatic action of the saliva appeared to be wholly destroyed, or at least nearly so. Repeated experiments tried in the manner already described, but without diluting the fluid after digestion, showed that in the concentrated fluid there was a slight reducing action, but the amount of sugar formed must have been exceedingly small. The low diastatic power of the saliva treated with .2 per cent. HCl for two hours was probably dependent in part on the neutral condition of the fluid, and possibly on the presence of the neutral salt

[1] In Herrmann's Handbuch d. Physiologie, Band 5, Theil 1, p. 113.

[2] Experiments now in progress in this laboratory point to a probable explanation of this fact.

formed by neutralization, but it seems more than probable that a part of the ferment was destroyed by the acid.

That the ferment ptyalin should be digested and thus destroyed by the acid solution of pepsin does not seem at all impossible. It is well known that the pancreatic trypsin is digested by gastric juice, and there is no evidence that the salivary ptyalin is less susceptible of change under like circumstances.

Thus it would seem from our experiments that the diastatic ferment of saliva is not only hindered in its action by the acidity of the gastric juice, but that it is, in part at least, destroyed, and thus debarred from any further part in the conversion of starch into sugar.

II.—*Products of Salivary Digestion.*

In order to study in detail the different products which result from the action of saliva on starch, several digestions were made with large quantities of material, the results of which were exceedingly satisfactory. 40 grams of starch made into a paste by boiling with 600 cc. water were digested with 200 cc. of filtered saliva for 15 hours at 40° C. The mixture was then evaporated to dryness on a water-bath, and the semi-dry residue treated with 700 cc. of 95 per cent. alcohol, which was allowed to remain in contact with it for 24 hours. The residue, which was mainly composed of unaltered starch, contained a body of strong reducing power and apparently dextro-rotary.

To the alcoholic solution 300 cc. of ether were added, and the mixture allowed to stand several days, at the end of which time quite a heavy gummy precipitate had settled out. The supernatant fluid was poured off and treated again with ether. After several days a second gummy precipitate formed, and by again adding a large quantity of ether to the solution a third colorless and gummy precipitate was obtained. By treating this filtrate with ether another precipitate gradually settled out, which, on standing a few days, was found to be composed wholly of small, white needle-like crystals.

This crystalline precipitate was washed with large quantities of ether and then dried over oil of vitriol, and finally at 112°C. until a constant weight was obtained. The dried crystals weighed 5.78 grams. A portion of the crystals was subjected to an analysis with the following result:

	I.	II.	III.	Calculated for $C_{12}H_{22}O_{11}$.
C	41.92	42.03	41.98	42.10
H	6.52	6.58	6.50	6.43
O				51.47

Thus in composition the crystals correspond very closely with maltose. Crystallized maltose contains 1 molecule of H_2O, which, however, is completely driven off at 112–115°C. The crystals under examination were very soluble in water, sweet to the taste, and possessed the power of reducing alkaline copper solutions. A solution of the crystals was found to be dextro-rotary. The specific rotary power of the dried substance as determined by Wild's polaristrobometer in a 200 millimeter tube was +148.95° for sodium light. The specific rotary power of pure maltose as determined by O. Sullivan is +150°, by E. Schulze +149.5°.[1] The relative reducing power of the substance determined by means of Fehling's solution in the manner already described was found to be 67–68; the reducing power of pure maltose being 66; that is, 100 parts of maltose reduce as much copper oxide as 66 parts of dextrose.

The above results then show very conclusively that the crystalline product is maltose, thus confirming the previous results of Musculus and Mering,[2] and likewise of Dr. E. H. Bimmerman[3] and E. Kulz.[4]

A portion of the last alcohol-ether filtrate from the maltose precipitate left on evaporation a small residue, which was dextro-rotary and possessed of strong reducing power, presumably dextrose, though it was not subjected to a careful examination.[5] The three syrupy or gum-like precipitates obtained previous to the maltose precipitate by the addition of ether were all dextro-rotary and possessed of reducing power.

[1] See Sundwik on the specific rotary power of pure maltose. Zeitschrift für Physiolog. Chem. 5, 427.

[2] Zeitschrift für Physiolog. Chem. 2, 403.

[3] Pflüger's Archiv. 20, 201. Also Report on Salivary Digestion in this Journal, 3, 221.

[4] Pflüger's Archiv. 24, 81.

[5] See Musculus and Mering.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

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(Continued from Vol. 2, p. 294.)

PHOSPHO-MOLYBDATES.

The application of molybdic oxide to the separation and estimation of phosphoric acid has given a special interest to the phospho-molybdates, and they have accordingly been studied more or less completely by several chemists. The most thorough investigations which we possess are those of Debray,[2] Rammelsberg,[3] and Finkener,[4] but particular salts have been examined by others, and these will be noticed under the appropriate special headings.

Phospho-molybdates appear to be formed whenever phosphoric acid or a soluble phosphate is brought into solution with a molybdate, the presence of a free acid not being essential. They are also formed when phosphates and molybdates are fused together, when molybdates insoluble in water are dissolved in phosphoric acid, when molybdic oxide is digested with an alkaline phosphate, and when insoluble phosphates and molybdates are treated together with a dilute acid. As a class, they are better defined and more easy to obtain pure than the phospho-tungstates, which in many respects they closely resemble. When phospho-molybdates of fixed alkaline bases are heated, they at first give off water of crystallization, and by careful heating may be obtained anhydrous. In some cases, however, molybdic oxide is volatilized even from salts containing fixed alkaline bases. I did not succeed in obtaining well-defined pyro-phospho-molybdates or pyro-phospho-tungstates, though of course the residues of the ignition of the acid salts may be regarded as such. When a phospho-molybdate is dissolved in ammonia-water and a current of sulphydric acid gas is passed into the hot solution, sulpho-molybdates are formed in large quantity. This reaction distinguishes the phospho-molybdates

[1] Proceedings Amer. Acad. of Arts and Sciences. Communicated by the Author.

[2] Bull. Soc. Chim. 2, 404.

[3] Berichte deutsch. chem. Gesellschaft, **10**, 1776.

[4] Ibid. **11**, 1638.

from the phospho-tungstates, which are not decomposed under the same circumstances.

Analytical Methods.—The determination of the sum of the percentages of molybdic and phosphoric oxides was usually effected, as in the case of the phospho-tungstates, by precipitating the two oxides together by mercurous nitrate, with addition of mercuric oxide to neutralize the free nitric acid. It is best to precipitate from a boiling solution, and to boil for a short time after adding mercuric oxide. This last must always be in small excess. On account of the volatility of molybdic teroxide, it is not possible to determine directly the sum of the weights of the two oxides by simple ignition, but the difficulty may be readily overcome by the following process. The filter with the mercurous salts is to be cautiously heated in a platinum crucible properly inclined to the vertical axis of the flame until the filter is completely carbonized. On then regulating the heat and the supply of air, the carbon may be readily burned off, leaving a mass of mercurous salts mixed with more or less mercuric oxide, no weighable amount of molybdic teroxide being lost. An accurately weighed quantity of anhydrous normal sodic tungstate in fine powder is then to be added, and the contents of the crucible carefully mixed together with a stout platinum wire previously weighed with the crucible itself. The whole is to be heated at first by radiation from a small iron dish, and afterward directly, until a clear white fused mass is obtained. A second ignition and second weighing will determine whether every trace of mercury has been expelled. It is almost needless to remark that all these operations must be conducted under a flue with a good draught. This process gives excellent results, and is much less tedious than would perhaps be supposed.

After the estimation of the phosphoric oxide, the molybdic teroxide is best determined by difference from the sum of the weights of the two oxides found as above. No really good general method for the quantitative separation and estimation of molybdic oxide has yet been given, at least no one which is sufficiently accurate to serve as a check upon the method above described. The ammonium salts of this series are most simply analyzed by igniting them directly with sodic tungstate, when the loss of weight corresponds to the sum of the water and ammonia.

As in the case of the phospho-tungstates, the quantitative determination of the phosphoric oxide is a matter of considerable

difficulty. The method of separation by means of magnesia mixture has been carefully studied by Dr. Gooch, to whose paper I have already referred.[1] Dr. Gooch found it necessary to precipitate the ammonio-magnesic phosphate a second time, a single precipitation giving an error amounting sometimes to 6 or 7 per cent. of the phosphoric acid present. After re-solution and precipitation by ammonia, the mean error amounted to only 0.65 per cent., which makes an almost insensible correction when the quantity of phosphoric oxide is small. In a few instances I have applied this correction after a double precipitation, but I prefer to employ the following method, which gives an almost perfect separation from molybdic teroxide. The phosphoric oxide is first precipitated from a hot solution as ammonio-magnesic phosphate, the supernatant liquid after complete subsidence carefully decanted upon an asbestos filter, the precipitate washed with magnesia mixture and ammonia, then redissolved in the least possible quantity of hot dilute chlorhydric acid and reprecipitated with ammonia. After complete subsidence and decantation, the precipitate is boiled with successive portions of a solution of ammonic sulphide. A more or less dark orange-red solution of ammonic sulpho-molybdate is always obtained at first, but after two or three repetitions of the process the ammonic sulphide added remains colorless on heating. The ammonio-magnesian phosphate is then filtered upon the asbestos filter already employed. In place of this method I have sometimes employed the following modification, which gives, I think, equally good results. After the first precipitation the phosphate is to be redissolved, and the hot solution precipitated at once by ammonic sulphide in excess. The precipitated phosphate is then to be boiled two or three times with ammonic sulphide as above. Whatever inaccuracy is inherent in this method depends, in my judgment, upon the fact that, as Dr. Gooch has shown, the determination of phosphoric acid by means of magnesia is, under the most favorable circumstances, a less accurate process than has been supposed.

The determination of ammonia and the alkalies was effected by the methods already described in the case of the phospho-tungstates. Water must be estimated by ignition with sodic tungstate, as there is often volatilization of molybdic teroxide when a phospho-molybdate is ignited at a temperature sufficient to expel its water.

[1] Proceedings of American Academy, **15**, 53; and this Journal, **1**, 391.

The analyses require great care and no small amount of practice to insure good results. As in the case of the phospho-tungstates, the alkaline bases are best determined by difference.

Twenty-four Atom Series.—Phospho-molybdic acid. The acid of this series was first obtained by Debray, who prepared it by boiling ammonic phospho-molybdate with nitro-muriatic acid, and allowing the solution to evaporate spontaneously. I find that this is a good method of obtaining the acid, but the following details should be observed. The bright yellow ammonic phospho-molybdate should be first dried, and then heated with a large excess of strong aqua-regia in a casserole over an iron capsule to serve as a radiator. In this manner the decomposition proceeds very regularly and without successions. When it becomes necessary to add fresh acid, the supernatant liquid should be allowed to settle completely and then be poured off carefully. Fresh acid may then be added, and the process, which is at best a slow one, continued. When the ammonium salt has disappeared, the liquid is to be evaporated until the excess of nitric and chlorhydric acids has been expelled. On standing, large bright yellow octahedral crystals are obtained from the very concentrated solution. These may be redissolved and recrystallized, but there is always some loss in the process of purification, because solution in water produces more or less decomposition of the acid with formation of a pale greenish white crystalline body. This substance passes very readily through a filter, and the solution of the acid must be allowed to settle completely before the clear supernatant liquid is brought upon the filter. Debray obtained three different hydrates of phospho-molybdic acid, to which he gave, respectively, the formulas

$$20MoO_3.P_2O_5.3H_2O + 21aq,$$

$$20MoO_3.P_2O_5.3H_2O + 48aq,$$

and

$$20MoO_3.P_2O_5.3H_2O + 38aq.$$

Unfortunately, he has not given either the methods or the complete results of his analyses. In the first hydrate he found 13.30 per cent., in the second 23.40 per cent., and in the third 19.60 per cent. of water.

I obtained the acid only in transparent octahedral crystals which had a bright yellow color. Of these crystals, dried by pressure with woolen paper,

0.9945 gram lost by ignition with WO_4Na_2 0.2362 gram=23.75 per cent. water.

1.4588 gram gave 0.0713 gram $P_2O_7Mg_2$=3.12 per cent. P_2O_5.

The analysis leads to the formula

$$24MoO_3.P_2O_5.3H_2O+59aq,$$

which requires:

		Calc'd.	Found.
$24MoO_3$	3456	73.31	73.13
P_2O_5	142	3.01	3.12
$62H_2O$	1116	23.68	23.75
	4714	100.00	

The phosphoric oxide was determined by double precipitation and treatment with ammonic sulphide. The molybdic oxide was estimated by difference. The crystallized acid effloresces so readily that the precise determination of the water is difficult. In a portion of the crystals which had effloresced in a very marked degree,—

0.9873 gram lost on ignition with WO_4Na_2 0.1760 gram=17.82 per cent. water.

2.2472 grams gave 0.1163 gram $P_2O_7Mg_2$=3.31 per cent. P_2O_5.

The ratio of the molybdic to the phosphoric oxide is, in this analysis, also 24 : 1; and, if we compute the results of both analyses for an anhydrous compound of the two oxides, we find:

		Calc'd.		
$24MoO_3$	3456	96.06	95.91	95 97
P_2O_5	142	3.94	4.09	4.03
	3598	100.00	100.00	100.00

The analyses leave, I think, no reasonable doubt as to the ratio of the two oxides. Phospho-molybdic acid therefore corresponds in composition with phospho-tungstic acid, the ratio of the two oxides being 24 : 1, as given by Finkener,[1] and not 20 : 1, as stated by Debray. With respect, however, to the number of atoms of water in the crystallized octahedral hydrate, I may remark that, while the analysis agrees best with the formula given,

$$24MoO_3.P_2O_5.3H_2O+59aq,$$

[1] *Loc. cit.*

it is much more probable that the acid really contains an atom less of water, and that its formula, apart from the question of basicity, is

$$24MoO_3.P_2O_5.6H_2O+55aq,$$

like

$$24WO_3.P_2O_5.6H_2O+55aq,$$

already described. This formula requires 23.38 per cent. water, instead of 23.75 per cent., as found. Debray found 23.40 per cent. As already stated, the crystals analyzed were dried by pressure with woolen paper after draining off a syrupy mother liquor, and may therefore not have been perfectly free from extraneous water. Finally, the analyses of Finkener led also to the formula with 61 atoms of water, and I shall adopt this as the definite constitution of the octahedral hydrate. Finkener's work has not yet been published in detail; but, from the abstract which he has given, it clearly appears that we owe to him the establishment of the true constitution of the only phospho-molybdic acid yet obtained. As already mentioned, there are two other hydrates of phospho-tungstic acid having respectively the formulas

$$24WO_3.P_2O_5.6H_2O+47aq,$$

and

$$24WO_3.P_2O_5.6H_2O+34aq.$$

The two hydrates of phospho-molybdic acid described by Debray would correspond to the formulas

$$24MoO_3.P_2O_5.6H_2O+24aq,$$

and

$$24MoO_3.P_2O_5.6H_2O+43aq,$$

if we suppose them, as is most probable, to belong to the 24-atom series. The first formula requires 13.05 per cent., the second 19.66 per cent. water. Debray found 13.09 per cent. and 19.60 per cent. Finkener obtained still another hydrate, containing about 32 atoms of water, basic water included.

Phospho-molybdic acid dissolves very readily in water, forming a colorless liquid which has a strong acid reaction. As already stated, the solution is always accompanied by a slight decomposition, with formation of a very pale greenish white crystalline substance. A precisely similar decomposition is observed in the

solution of the corresponding phospho-tungstic acid. The crystals lose all their water when slightly ignited. According to Finkener, three atoms of water remain at 140°C. The solution readily expels carbonic dioxide from the alkaline carbonates. The question of the basicity of the acid will be discussed farther on.

24 : 3 *Ammonic Phospho-molybdate.*—The constitution of the beautiful yellow salt which is formed when an excess of a mineral acid is added to a solution containing molybdic and phosphoric oxides and a salt of ammonium, has long been in dispute. The analyses of Svanberg and Struve,[1] Nutzinger,[2] Sonnenschein,[3] Lipowitz,[4] and Seligsohn,[5] gave results which differed very sensibly from each other, according to the method of analysis employed. Debray gave the formula

$$20MoO_3.P_2O_5.3(NH_4)_2O+3aq,$$

but without the details of his analysis. More recently the subject has been examined with great care by Finkener,[6] who has arrived at the conclusion that, though the percentages of water and ammonia may vary within wide limits, the ratio of the molybdic and phosphoric oxides is always as 24 : 1.

With respect to the preparation and properties of the yellow ammonium salt, I have little to add to what has been done by these chemists. I repeatedly prepared the salt for analysis, usually by mixing solutions of ammonic molybdate—7 : 3 salt—and phosphate, adding nitric acid in excess to the solution, and boiling. When the mixed solution is boiled for a short time, the precipitation of the yellow salt is complete after standing until the liquid becomes cold. In the publication of this result, which is important in analysis, I have been anticipated by Atterberg;[7] but I propose in another paper to give the results of my work on the quantitative determination of phosphoric acid, and will then give ample details.

As regards the composition of the yellow phospho-molybdates of ammonium, my results do not agree with those of Finkener, as I think I have evidence that, as in the case of the phospho-tungstates, there are series of phospho-molybdates in which the ratio

[1] Journal für prakt. Chemie, **44**, 291.
[2] Pharmaceut. Vierteljahresschrift, **4**, 549.
[3] Journal für prakt. Chemie, **53**, 342.
[4] Poggendorff's Annalen, **109**, 135.
[5] Journal für prakt. Chemie, **67**, 470.
[6] *Loc. cit.*
[7] Berichte deutsch. chem. Gesellschaft, **14**, 1217.

of the molybdic to the phosphoric oxide is as 20 : 1, as 22 : 1, and as 24 : 1. In one preparation—

1.1492 gram lost on ignition with WO_4Na_2 0.0827 gram NH_3 and H_2O=7.20 per cent.

0.5905 gram lost on ignition with WO_4Na_2 0.0432 gram NH_3 and H_2O = 7.31 per cent.

1.7158 gram gave 0.1027 gram $P_2O_7Mg_2$ = 3.83 per cent. P_2O_5.

0.9806 gram gave 0.0567 gram $P_2O_7Mg_2$ = 3.70 per cent. P_2O_5.

1.8903 gram gave 0.1321 gram NH_4Cl = 3.20 per cent. $(NH_4)_2O$.

In these analyses the first determination of the phosphoric oxide was made by double precipitation only, without subsequent treatment with ammonic sulphide; but in the second, this reagent was employed in the manner above described. The ratio of MoO_3 to P_2O_5 is almost precisely 24 : 1, and the analyses correspond closely with the formula

$24MoO_3.P_2O_5.3(NH_4)_2O + 24MoO_3.P_2O_5.2(NH_4)_2O.H_2O + 16aq$, which requires :

		Calc'd.	Mean.		
$48MoO_3$	6912	89.05	89.00	...	...
$2P_2O_5$	284	3.66	3.75	3.70	3.83
$5(NH_4)_2O$	260	3.35	3.39	3.39	
$17H_2O$	306	3.94	3.86	3.81	3.92
	7762	100.00	100.00		

Acid salts of similar type occur frequently in the class of phosphomolybdates, as in that of phospho-tungstates.

24 : 1 *Croceo-cobalt Salt.*—The disposition of the cobaltamines to form highly crystalline compounds, together with their well-defined and various degrees of basicity, led me to study the relations of these bases to the phospho-molybdic acids. This had already been done to a certain extent with the 5 : 1 atom series by Jörgensen, whose results I shall cite in connection with that series. Neither roseo-cobalt nor luteo-cobalt forms well-defined salts with 24 : 1 phospho-molybdic acid. I had therefore recourse to croceo-cobalt,[1] the oxide of which may be written

$$Co_2(NH_3)_8(NO_2)_4O, \text{ or, briefly, } CcO.$$

The chloride of this series gives no precipitate with solutions of 7 : 3 ammonic molybdate, or of hydro-disodic phosphate; but in an

[1] Proceedings of American Academy, **10**, 1.

acid solution of these two salts a solution of the chloride throws down a beautiful bright yellow highly crystalline salt, which may be washed with cold water. The portion analyzed was dried on woollen paper only. Of this salt—

1.0728 gram gave 0.8133 gram $MoO_3+P_2O_5=75.81$ per cent.

1.4520 gram gave 0.4719 gram $P_2O_5=2.96$ per cent.

This corresponds to 72.85 per cent. MoO_3 by difference, and 24.19 per cent. of CcO and water by the loss. The analyses agree very closely with the formula

$$24MoO_3.P_2O_5.CcO.2H_2O+21aq,$$

which requires:

		Calc'd.		
$24MoO_3$	3456	72.82		72.86
P_2O_5	142	2.99		2.96
CcO	734	15.47	24.19	24.19
$23H_2O$	414	8.72		
	4746	100.00		

Under the microscope this salt is seen to consist of fine yellow felted needles. It is very slightly soluble in cold water, but is soluble in a rather large quantity of boiling water, giving an orange yellow solution, with a strongly acid reaction. The solution gives with argentic nitrate a very insoluble sulphur-yellow flocky precipitate, which after a time becomes crystalline, and a pale yellow flocky precipitate with mercurous nitrate. No precipitate is formed with cupric sulphate or baric chloride. The salt could not be recrystallized; it is interesting as a particularly well-defined soluble acid salt of the 24 : 1 atom series.

24 : 2 *Acid Potassium Salt.*—This salt was prepared by boiling together solutions of potassic molybdate and phosphate, adding an excess of nitric acid, and boiling the whole for some time. As in the case of the ammonium salts, the precipitation is greatly facilitated by this process, taking place very slowly in the cold. The salt obtained was in very minute crystals, bright yellow, and but slightly soluble in cold water. Of this salt—

0.7772 gram lost on ignition 0.0128 gram = 1.64 per cent. water.
0.7962 " " 0.0130 " = 1.66 " "
1.1703 gram gave 1.0895 gram $MoO_3+P_2O_5=93.10$ per cent.
1.3263 gram gave 0.0779 gram $P_2O_7Mg_2=3.76$ per cent. P_2O_5.
1.3033 gram " 0.0778 gram " = 3.82 " "

The phosphoric oxide was twice precipitated as ammonio-magnesic phosphate. The analyses correspond with the formula

$$24MoO_3.P_2O_5.2K_2O.H_2O+3aq,$$

which requires:

		Calc'd.			
$24MoO_3$	3456	89.55		89.31	
P_2O_5	142	3.69	3.76		3.82
$2K_2O$	189	4.90		5.25	
$4H_2O$	72	1.86	1.66		1.64
	3859	100.00			

Twenty-two Atom Series.—In the paper already referred to, Rammelsberg has described several salts in which he found the ratio of molybdic to phosphoric oxide as 22 : 1. Unfortunately, he has not given the method of analysis which he employed, and in a question of so much difficulty and delicacy it is, to say the least, extremely desirable to know what degree of precision may be expected in the analyses. As his results appear to be supported by my own, I shall adopt them, leaving to the further progress of analytical chemistry the final settlement of the few doubtful points.

22 : 3 *Ammonium Salt.*—Rammelsberg found for the neutral salt of this series the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O+12aq,$$

which corresponds, except as regards the amount of water of crystallization, with a phospho-tungstate which I have already described—

$$22WO_3.P_2O_5.3(NH_4)_2O+21aq.$$

In one preparation of a yellow insoluble ammonium salt exactly resembling the corresponding salt of the 24-atom series—

1.6885 gram lost on ignition with WO_4Na_2 0.0873 gram = 5.17 per cent. NH_3 and H_2O.

1.7764 gram gave 0.6200 gram $P_2O_7Mg_2$ = 4.17 per cent. P_2O_5.
1.9024 gram " 0.6029 gram " = 4.01 " "
1.2334 gram " 0.6262 gram NH_4Cl = 4.23 " $(NH_4)_2O$.

The salt was dried for some time *in pleno* over sulphuric acid, and had evidently lost water of crystallization. If we deduct the

remaining water, 0.94 per cent., and calculate the analysis for an anhydrous salt, we have for the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O\,;$$

		Calc'd.	
$22MoO_3$	3168	91.41	91.68
P_2O_5	142	4.09	4.05
$3(NH_4)_2O$	156	4.50	4.27
	3466	100.00	

In another preparation—

1.0324 gram lost on ignition with WO_4Na_2 0.0922 gram = 8.93 per cent. NH_3 and H_2O.

2.0670 grams gave 0.1255 gram $P_2O_7Mg_2$ = 3.88 per cent. P_2O_5.
2.0352 grams " 0.1226 gram " = 3.84 " "

These analyses lead to the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O + 9aq,$$

which requires

		Calc'd.			
$22MoO_3$	3168	87.32		87.21	
P_2O_5	142	3.91	3.88		3.84
$3(NH_4)_2O$	156	4.29	8.77	8.93	
$9H_2O$	162	4.48			
	3628	100.00			

If, from the analyses of the two salts above described, we calculate the composition of the combination of molybdic and phosphoric oxides supposed to be isolated, and compare this with the percentages calculated upon the two hypotheses of a ratio of 22 : 1 and a ratio of 24 : 1, we have—

		Calc'd.	I.	II.	Calc'd.		
$22MoO_3$	3168	95.76	95.76	95.76	96.06	3456	$24MoO_3$
P_2O_5	142	4.24	4.24	4.24	3.94	142	P_2O_5
	3310	100.00	100.00	100.00	100.00	3598	

In both cases the phosphoric acid was precipitated twice, but the ammonia-magnesian phosphate was not treated with ammonic

sulphide. According to the results of Dr. Gooch already cited, the probable error of this method does not exceed 1 per cent. in excess of the quantity of phosphoric oxide present. It appears, therefore, that the correction to be applied to the phosphoric oxide in the above analyses does not, at most, exceed 0.04 per cent. The mean of Dr. Gooch's analyses would require a deduction of 0.02 per cent. only. The yellow ammonium salt analyzed by Rammelsberg corresponds to the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O + 12aq,$$

which requires (Rammelsberg)—

		Calc'd.	
$22MoO_3$	3168	86.04	86.45
P_2O_5	142	3.85	3.90
$3(NH_4)_2O$	156	4.24	3.25
$12H_2O$	216	5.86	5.77
	3682	100.00	99.37

Rammelsberg gives these figures as the means of several analyses which agree well with each other, but it must be admitted that a closer correspondence with the percentages required by the formulas would have been desirable. The comparison is not given in his paper. The air-dried salt loses all its water over sulphuric acid. The three atoms of basic water, if we assume their existence, must therefore be united by a very feeble affinity. Rammelsberg has also analyzed the corresponding potassic salt of the same series. I here give his results for the sake of comparison with the formula:

		Calc'd.	
$22MoO_3$	3168	83.17	84.43
P_2O_5	142	3.73	3.78
$3K_2O$	283	7.43	6.86
$12H_2O$	216	5.67	5.55
	3809	100.00	100.62

This salt loses all its water between 120° and 140°. In judging the results of these analyses, as well as of those which I have given, it must be carefully borne in mind that the salts themselves cannot be recrystallized, and that consequently their absolute purity cannot

be guaranteed. Moreover, if—as I believe I have shown—there are very similar salts which represent three series in which the ratios of the molybdic and phosphoric oxides are respectively as 24 : 1, 22 : 1, and 20 : 1, we may, at least occasionally, have mixtures of the salts of three, or of any two series. The difficulty here is precisely that which occurs in the case of the phospho-tungstates.

44 : 2 *Acid Potassium Salt.*—This salt was prepared by boiling a mixture of potassic molybdate and phosphate with nitric acid in excess, when a beautiful yellow crystalline powder separated. This was washed with cold water and dried on woollen paper. Of this salt—

0.9850 gram lost on ignition 0.0521 gram = 5.28 per cent. water.
0.8983 gram gave 0.7943 gram $MoO_3+P_2O_5$ = 88.42 per cent.
2.0617 grams gave 0.1201 gram $P_2O_7Mg_2$ = 3.72 per cent.
These analyses lead to the formula

$$44MoO_3.2P_2O_5.5K_2O.H_2O+21aq,$$

or

$$22MoO_3.P_2O_5.3K_2O+22MoO_3.P_2O_5.2K_2O.H_2O+21aq,$$

which requires

		Calc'd.	
$44MoO_3$	6336	84.62	84.70
$2P_2O_5$	284	3.79	3.72
$5K_2O$	472	6.30	6.30 (diff.)
$22H_2O$	396	5.29	5.28
	7488	100.00	

The salt is therefore the acid salt corresponding to a neutral salt with the formula

$$22MoO_3.P_2O_5.3K_2O.$$

Rammelsberg's analyses agree better with the formula of the acid salt given above than with that of the neutral compound assumed by him.

Twenty Atom Series.—The only salt of this series which I have obtained is one of ammonium prepared like the salts already described, having like these a fine yellow color and a very fine grained crystalline structure, and, like them, but slightly soluble in water. Of this salt—

1.0936 gram lost on ignition with WO_4Na_2 0.0729 gram = 6.66 per cent. NH_3 and H_2O.

1.8183 gram lost on ignition with WO_4Na_2 0.1155 gram = 6.35 per cent. NH_3 and H_2O.

0.8862 gram gave 0.6153 gram NH_4Cl = 4.12 per cent. $(NH_4)_2O$.

1.3213 gram gave 0.6224 gram $P_2O_7Mg_2$ = 4.19 per cent. P_2O_5.

1.5135 gram gave 0.6349 gram $P_2O_7Mg_2$ = 4.31 per cent. P_2O_5.

The salt was dried on a water bath, and afterward over sulphuric acid. The phosphoric oxide was precipitated twice, but not treated with ammonic sulphide. The analyses led to the formula

$$60MoO_3.3P_2O_5.8(NH_4)_2O.H_2O+11aq,$$

which requires—

		Calc'd.				
$60MoO_3$	8640	89.09	93.48	89.21		93.52
$3P_2O_5$	426	4.39		4.31	4.19	
$8(NH_4)_2O$	416	4.29	6.52	4.12		6.50
$12H_2O$	216	2.23		2.54		
	9698	100.00				

If we calculate the composition of the mixed oxides of molybdenum and phosphorus existing in this salt, we have—

		Calc'd.	
$20MoO_3$	2880	95.30	95.39
P_2O_3	142	4.70	4.61
	3022	100.00	100.00

It will be seen that the ratio is here very nearly as 20 : 1. This may however be merely accidental, and farther researches are necessary to fully establish the existence of a 20-atom series.

According to Debray a solution of argentic nitrate gives with one of phospho-molybdic acid a precipitate which soon becomes crystalline, and which has the formula

$$20MoO_3.P_2O_5.7Ag_2O+24aq.$$

Such a salt would possess a twofold interest, first, as another evidence of the existence of a 20-atom series of phospho-molybdates, and, secondly, as showing that the acid of the series may unite with more than *six* atoms of base. On mixing the two solutions as above, I obtained a precipitate in small indistinct crystals of a greenish yellow color. These crystals were soluble in hot water,

but the solution was quickly decomposed with precipitation of a white powder. Under the microscope with a high power and transmitted light the salt appeared to consist of small tabular crystals mixed with a few long yellow prisms of very different habitus. Of this compound—

1.3604 gram lost by ignition with WO_4Na_2 0.0692 gram water = 5.08 per cent.

2.1099 grams gave 0.8287 gram AgCl = 31.63 per cent. Ag_2O.

0.6733 gram gave 0.2619 gram AgCl = 31.44 per cent. Ag_2O.

2.1099 grams gave 0.0928 gram $P_2O_7Mg_2$ = 2.81 per cent. P_2O_5.

The phosphoric oxide was determined in the filtrate from the argentic chloride by double precipitation and treatment with ammonic sulphide. The ratio of the molybdic to the phosphoric oxide is as 21 : 1, but the formula which most nearly represents the analysis is

$$22MoO_3.P_2O_5.7Ag_2O+14aq,$$

which requires

		Calc'd.		
$22MoO_3$	3168	61.08	60.57	
P_2O_5	142	2.74	2.81	
$7Ag_2O$	1624	31.32	31.44	31.63
$14H_2O$	252	4.86	5.08	
	5186	100.00		

The only conclusion which can fairly be drawn from the analysis is that there is at least one phospho-molybdate in which the number of atoms of base exceeds three. It is certain that the salt does not represent a perfectly definite and homogeneous compound, and it may possibly be a mixture of the 20-atom salt, $20MoO_3.P_2O_5.6Ag_2O$, and an acid molybdate of silver, $2MoO_3.Ag_2O$, nearly in atomic proportions. By dissolving the salt in nitric acid and evaporation, Debray obtained another salt in small brilliant yellow crystals. For this salt he proposes the formula

$$20MoO_3.P_2O_5.2Ag_2O+7aq,$$

but as usual he has given no analyses.

Eighteen Atom Series.—I have myself met with no salts belonging to this series, but according to Finkener[1] there are sodium salts corresponding to the general formula

$$18MoO_3.P_2O_5(3-x)Na_2O+(25+x)aq.$$

These salts are yellow and easily soluble.

[1] *Loc. cit.* p. 1639.

Sixteen Atom Series.—16 : 3 Ammonium Salt. In preparing the 5 : 3 atom ammonium salt a white crystalline precipitate was formed, insoluble in cold, but soluble with decomposition in much boiling water, and easily soluble in ammonia. In this salt dried over sulphuric acid,—

0.5100 gram lost by ignition with WO_4Na_2 0.0722 gram = 14.16 per cent. NH_3 and H_2O.

1.1653 gram gave 0.1259 gram NH_4Cl = 5.25 per cent. $(NH_4)_2O$.

0.8114 gram gave 0.0658 gram $P_2O_7Mg_2$ = 5.19 per cent. P_2O_5.

The analysis corresponds with the formula

$$16MoO_3.P_2O_5.3(NH_4)_2O + 14aq,$$

which requires

		Calc'd.	Found.
$16MoO_3$	2304	80.73	80.65
P_2O_5	142	4.97	5.19
$3(NH_4)_2O$	156	5.46	5.25
$14H_2O$	252	8.84	8.91
	2854	100.00	

(*To be continued.*)

Contributions from the Chemical Laboratory of Harvard College.

XIV.—PYROXANTHIN.[1]

By Henry B. Hill.

I have mentioned in an earlier paper[2] the yellow flocculent precipitate formed by the action of alkalies upon the crude furfurol, which upon examination proved to consist chiefly of pyroxanthin. This substance was discovered in 1835 by Dr. Scanlan,[3] of Dublin, in the residue from the preparation of methyl alcohol from crude wood spirit by means of lime. In 1836 it was further studied by Apjohn and Gregory,[4] who deduced from their analyses the for-

[1] Proceedings Amer. Academy of Arts and Sciences. Communicated by the Author.
[2] This Journal, **3**, 37.
[3] Phil. Mag. [3] **41**, 395.
[4] Royal Irish Acad. Proc. 1836, **33**. Ann. Chem. u. Pharm. **21**, 143.

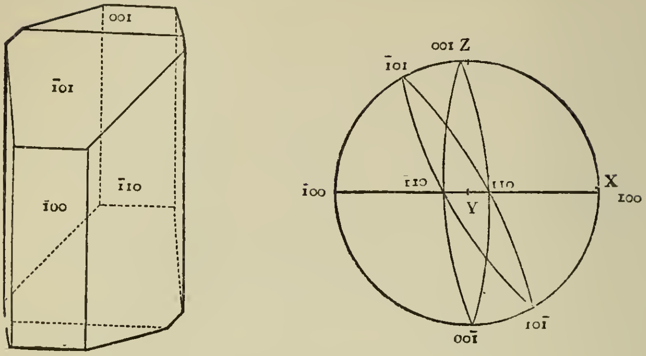
mula $C_{21}H_{18}O_4$, although they did not succeed in confirming this formula by the preparation and analysis of any of its derivatives. This formula was subsequently changed to $C_{10}H_8O_2$ by Gmelin,[1] although this change was apparently not based upon any further experimental work. Although I have not as yet had any very considerable quantity of material at my command, I have studied some of its reactions, and prepared two well-marked bromine derivatives whose percentage composition necessitates the adoption of the formula $C_{15}H_{12}O_3$.

In the method I have described for the purification of the crude furfurol, after that portion which is volatile with steam has been distilled off, there remains a red viscous oil in the retort, which, on cooling, partially solidifies. If this semi-solid mass is then treated with small quantities of cold alcohol, the red oil, which results, in part at least, from the action of the sodic hydrate upon the furfurol, dissolves, while the greater part of the pyroxanthin is left behind in minute crystals. Occasionally, this viscous residue crystallizes only after the addition of the alcohol and vigorous stirring. The pyroxanthin seems to be more neatly separated, if the furfurol is slightly acidified with acetic acid after separating the alkaline solution before distilling with steam. After the crystals have been well washed with cold alcohol, they are recrystallized from boiling alcohol until the substance has a bright, clear, orange-yellow color. Boiling the alcoholic solution with bone-black facilitates the removal of the red impurities.

Pyroxanthin is completely insoluble in water, and very sparingly soluble in ether or carbonic disulphide; in hot alcohol, benzol, or glacial acetic acid it dissolves abundantly, and crystallizes in well-developed forms on cooling. From alcohol it crystallizes in small, brilliant, orange-yellow needles with a blue reflex; from benzol in tolerably large reddish-yellow monoclinic prisms; and from glacial acetic acids in flat radiated needles, which are formed by the development of the prism in the direction of the orthodiagonal. The crystallographic examination which I made of the substance gave the following results:

[1] Gmelin's Handbuch, 7, 157.

CRYSTALLINE FORM OF PYROXANTHIN.



Monoclinic System.

Forms observed {001} {$\bar{1}$01} {10$\bar{1}$} {110}.

$a : b : c = 2.748 : 1 : 1.413 \quad ac = 87° \; 56'$

Angles between Normals.

	Found.	Calculated.
110 : $\bar{1}$10	40° 1'	Fundamental angles.
$\bar{1}$01 : 001	26° 46'	
$\bar{1}$01 : $\bar{1}$00	61° 10'	
110 : 00	69° 54'	69° 59'
$\bar{1}$10 : $\bar{1}$01	80° 25'	80° 30'

For analysis the substance was crystallized from alcohol and dried at 100°.

I. 0.2673 gram substance gave 0.7341 gram CO_2 and 0.1279 gram H_2O.

II. 0.2432 gram substance gave 0.6690 gram CO_2 and 0.1841 gram H_2O.

	Calculated for $C_{15}H_{12}O_3$.	Found. I.	Found. II.	Apjohn and Gregory.
C	75.00	74.91	75.01	74.27
H	5.00	5.31	5.25	5.61

Since the substance was very refractory and needed a high temperature in a stream of oxygen for complete combustion, my results

show a sufficiently close agreement with those of Apjohn and Gregory.

This substance melts at 162° and volatilizes with partial decomposition at a higher temperature, although it may be sublimed without difficulty by careful heating in a current of air. In concentrated sulphuric acid it dissolves with an intense purple, and in hydrochloric or hydrobromic acid with a crimson color. From these solutions water precipitates the substance apparently unchanged. In alkaline solutions it is completely insoluble, and by melting caustic potash it is merely carbonized. Bromine attacks it vigorously, and, under certain conditions, forms well-crystallized products.

Dibrompyroxanthintetrabromide, $C_{15}H_{10}Br_2O_3Br_4$. When pyroxanthin is suspended in ten times its weight of carbonic disulphide, and three and a half parts of bromide diluted with an equal weight of carbonic disulphide are added, the pyroxanthin instantly dissolves and forms a clear deep-red solution. After standing for a short time, clouds of hydrobromic acid are given off, and soon after the separation of a beautifully crystalline substance begins. After twenty-four hours the carbonic disulphide is poured off, and the crystals which have separated are thoroughly washed with ether. For analysis I recrystallized the substance from boiling chloroform and dried it *in vacuo*.

I. 0.5598 gram substance gave 0.5136 gram CO_2 and 0.0842 gram H_2O.

II. 0.6814 gram substance gave 0.5758 gram CO_2 and 0.0845 gram H_2O.

III. 0.3094 gram substance gave 0.4884 gram AgBr.[1]

IV. 0.3128 gram substance gave 0.4936 gram AgBr.

	Calculated for $C_{15}H_{10}Br_6O_3$.	Found. I.	II.	III.	IV.
C	25.07	25.02	24.87		
H	1.39	1.67	1.49		
Br	66.85			67.16	67.13

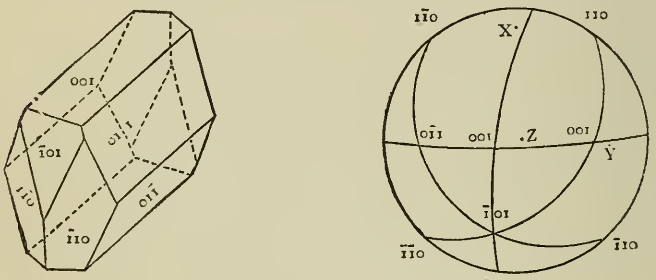
These percentages agree closely with those required by the formula $C_{15}H_{10}Br_6O_3$, and the behavior of the substance is such that it must be considered dibrompyroxanthintetrabromide. It crystallizes in small, brilliant, colorless prisms which belong to the triclinic system. On heating, it is decomposed below 100° with carbonization and the evolution of hydrobromic acid. It is very sparingly

[1] See note, 3, 42.

soluble in ether or carbonic disulphide; in boiling benzol or chloroform it dissolves quite freely, and the greater part again separates on cooling. In cold alcohol or glacial acetic acid, it is sparingly soluble; but, on warming, it dissolves with decomposition and then forms a yellow solution. In the cold, it is unaltered by concentrated sulphuric acid; on heating, it is carbonized.

A crystallographic study of the substance gave the following results:

CRYSTALLINE FORM OF DIBROMPYROXANTHINTETRABROMIDE.



Triclinic System.

Forms observed, $\{001\}$ $\{011\}$ $\{01\bar{1}\}$ $\{110\}$ $\{\bar{1}10\}$ $\{\bar{1}01\}$.

$a : b : c = 0.733 : 1 : 2.370.$

$bc = 74° 43'$; $ac = 83° 40'$; $ab = 96° 46'$.

Angles between Normals.

	Found.		Calculated.
$0\bar{1}1 : \bar{1}\bar{1}0$	47° 15′		
$0\bar{1}1 : \bar{1}01$	69° 50′		
$0\bar{1}1 : 011$	135° 27′	Fundamental angles.	
$\bar{1}\bar{1}0 : \bar{1}01$	34° 18′		
$\bar{1}\bar{1}0 : \bar{1}10$	76° 57′		
$\bar{1}01 : \bar{1}10$	48° 49′		48° 58′
$\bar{1}10 : 01\bar{1}$	61° 14′		61° 12′
$\bar{1}10 : 011$	58° 6′		57° 41′
$001 : \bar{1}\bar{1}0$	73° 59′		74° 18′
$001 : \bar{1}10$	93° 8′		93° 41′
$001 : 0\bar{1}1$	54° 6′		53° 49′
$001 : 011$	81° 21′		81° 38′
$001 : 101$	63° 37′		63° 57′

Bromine when moderately diluted with carbonic disulphide has no further action upon this substance. It is attacked, however, when exposed to the vapors of bromine, and deliquesces rapidly, forming a dark-red syrup, which over lime *in vacuo* gradually solidifies. From this product I have as yet been unable to isolate any substance with characters sufficiently well marked to encourage further study.

Dibrompyroxanthin, $C_{15}H_{10}Br_2O_3$. The subtraction of bromine, on the other hand, gave a beautifully crystalline product with sharply marked characteristics. This substance I first made by the action of phenol. If the dibrompyroxanthintetrabromide is gently warmed with a little phenol, to which sufficient water has been added to keep it liquid, it dissolves, forming a highly colored solution, which is red by transmitted and green by reflected light. If alcohol is then added, it causes the separation of an abundance of fine, felted brilliant-yellow needles, which may be recrystallized from alcohol. This same substance may also be made by boiling the tetrabromide with absolute alcohol, and adding zinc dust or finely powdered metallic antimony. The latter method is perhaps most advantageous, since little or no product is obtained if the phenol solution is too strongly heated, or if the zinc dust contains a large percentage of oxide. For analysis, the substance was dried at 100° after several recrystallizations from alcohol. The material used in analyses I. and II. was made with phenol, while that used in analysis III. was made with antimony.

I. 0.3816 gram substance gave 0.6333 gram CO_2 and 0.0918 gram H_2O.

II. 0.3137 gram substance gave 0.2978 gram AgBr.

III. 0.2577 gram substance gave 0.2419 gram AgBr.

Calculated for $C_{15}H_{10}Br_2O_3$.		Found. I.	II.	III.
C	45.22	45.25		
H	2.51	2.67		
Br	40.20		40.40	39.94

The analyses showed that the substance was dibrompyroxanthin, and that it was formed from the bromine derivative already described by the subtraction of bromine.

In hot alcohol it dissolves readily, although in cold it is sparingly soluble. It is quite soluble in ether or carbonic disulphide, and very readily in benzol, chloroform, or glacial acetic acid.

From a solution in warm chloroform, it crystallizes in large, compact, twinned forms of the monoclinic system, which are dichroic. In concentrated sulphuric acid, it dissolves with an intense, pure blue color. This blue solution, on dilution with water, throws down a yellow precipitate, which is apparently the unchanged substance. If quickly heated upon platinum foil, it melts to a perfectly clear yellow liquid; but it is impossible to determine its melting point, since it decomposes and carbonizes when its temperature is more gradually raised. A solution in carbonic disulphide, when mixed with bromine, gradually deposits well-formed crystals of the tetrabromide. This simple substitution product I have not succeeded in making directly from pyroxanthin. In every case where a smaller quantity of bromine was employed, the addition product was still formed, and a part of the pyroxanthin remained unaltered.

I have also studied the action of aqueous bromine, but have not been successful in obtaining any definite products. If pyroxanthin is suspended in water, and bromine gradually added, or the vapors of bromine carried in by a current air, a white amorphous substance is slowly formed, which is almost insoluble in water, but extremely soluble in other ordinary solvents. By evaporation of such solutions, the substance again separates in an amorphous condition. In alkalies it dissolves, forming a deep-brown solution, from which nothing can be precipitated by the addition of acids.

Since there appeared to be little hope of effecting its purification by ordinary methods, I proceeded to analyze carefully prepared material. I found, however, that the substance turned brown on standing over sulphuric acid, and the analysis of two different preparations showed conclusively that no constant results could be obtained in this way.

I. 0.3726 gram substance gave 0.3142 gram CO_2 and 0.0594 gram H_2O.

II. 0.2016 gram of the same preparation gave 0.2773 gram AgBr.

III. 0.5255 gram substance gave 0.4142 gram CO_2 and 0.0734 gram H_2O.

IV. 0.3853 gram of the same preparation gave 0.5731 gram AgBr.

	I.	II.	III.	IV.
C	23.00		21.50	
H	1.77		1.55	
Br		58.53		63.30

These results showed merely that oxidation had taken place together with the substitution of hydrogen by bromine.

On boiling with bromine-water, total decomposition seemed to ensue, and no definite products could be isolated except oxalic acid and a small quantity of a volatile oil which had the odor of bromoform, and gave the characteristic odor of phenyl isocyanide when heated with anilin and alcoholic potash.

Although I have already carried on the investigation of pyroxanthin in several other directions, I have not as yet been able to study the reactions involved as much in detail as I could wish, and I must therefore reserve for a subsequent paper all description of these experiments.

Concerning the origin and mode of formation of the pyroxanthin, I can at present add nothing. Its high melting point, and its general behavior when compared with the properties of the oil from which it is made, lead directly to the conclusion that it results either from polymerization or condensation. Its formula, $C_{15}H_{12}O_3$, naturally suggests a trimolecular polymeric form; the composition of its bromine derivatives, on the other hand, favors rather the view that its molecule is the product of condensation.

Schweizer,[1] in 1848, prepared from pyroligneous acid an oil to which he gave the name pyroxanthogen, as the substance from which the pyroxanthin was formed. He attempted no explanation of the mode of formation, and made no analysis of his product. Although his description is not very precise, it is sufficient to show that it was a mixture tolerably complex in its nature.

All my own attempts to isolate from the crude furfurol the substance essential to the formation of the pyroxanthin have been unsuccessful. Its separation from the furfurol is a matter of some difficulty, not only on account of the small quantities present, but also since it appears to be closely allied to furfurol. In its boiling point or in its behavior towards reagents, I have as yet found no differences sufficiently well marked to form the basis for a method of separation.

For the present, at least, a more careful study of the pyroxanthin itself would seem to be the most speedy way to discover the mode of its formation.

[1] Jour. pract. Chem. **44**, 129.

Laboratory Notes from the University of Cincinnati.

XXIII.—THE SPEED OF SAPONIFICATION OF ETHYL ACETATE.[1]

By R. B. Warder.

The term saponification, in its general sense, implies the separation of the alcoholic and the acid radical of a compound ether. For example, acetic ether may be decomposed by various means as follows:

1. $C_2H_5.O.C_2H_3O+HOH=C_2H_5OH+HOC_2H_3O.$
2. $C_2H_5.O.C_2H_3O+Na_2CO_3+H_2O$
$=C_2H_5OH+NaOC_2H_3O+HNaCO_3.$
3. $C_2H_5.O.C_2H_3O+HNaCO_3=C_2H_5OH+NaOC_2H_3O+CO_2.$
4. $C_2H_5.O.C_2H_3O+NaOH=C_2H_5OH+NaOC_2H_3O.$

The first of these reactions has already received some attention, directly and indirectly, in connection with experimental and theoretical researches on the speed and limits of etherification.[2] The study of the second reaction would doubtless be complicated by the third; and by the thermal relations of CO_2 to the solvent employed. The sesquicarbonate may give rise to still another simultaneous reaction. The saponification by sodic hydrate, although too rapid for the most convenient and accurate study, appears to represent a single metathetical operation; and the fourth reaction was accordingly selected for this part of the present research.

I.—Method of Experiment.

Dilute aqueous solutions of ethyl acetate and sodic hydrate, of known strength and volume, were quickly mixed together. At the end of a suitable interval, the alkali still remaining was quickly neutralized with excess of standard oxalic acid. The volume of acid required shows at once the amount of alkali present when the

[1] Some of the results contained in this paper have also appeared in Ber. **14**, 1361, and in this Journal, **3**, 203 and 294.

[2] See Berthelot and St. Gilles, Ann. chim. phys. [3] **65**, 385; **66**, 5; **68**, 225. Berthelot, Ann. chim. phys. [3] **66**, 110; [5] **14**, 437; **15**, 220. J. H. van't Hoff, Ber. **10**, 669. Menschutkin, Ann. Chem. **195**, 334; **197**, 193.

action was interrupted; whence the quantities of alkali and ether that have neutralized each other are found by difference. In making several determinations with the same mixture (as in Series I. and II., below), successive portions were drawn off to be neutralized at convenient intervals.

The absorption of carbon dioxide, by diminishing the intensity of the reaction, proved to be a source of error requiring special precautions. The soda solution was kept in a large bottle provided with soda-lime ventilator, and a syphon, through which it was drawn into the outlet of an ordinary burette. The latter was protected in the same manner, so that the alkali was completely shielded from the atmosphere, until it was measured from the burette into the experimental flask, to be mixed with the ether. This flask was likewise provided with soda-lime ventilator, and with a discharge pipe, through which successive portions were measured out with the pipette, without the admission of non-purified air.

It was not practicable to use a perfectly caustic soda solution, as usually prepared for alkalimetry with excess of calcic hydrate, because the still undetermined rate of saponification by lime would have complicated the problem. I therefore selected a nearly pure sample of soda, and made frequent determinations of its causticity. The distilled water used in dilution also contained traces of carbon dioxide, the effect of which was eliminated from the final results. Preliminary experiments showed that the direct action of water and small quantities of sodic carbonate, at ordinary temperatures, may be neglected in determinations of the far more rapid action of sodic hydrate. The titrations were made with phenol phthalein as indicator, by a method (similar to that of Lux[1]) which was expressly investigated[2] to meet the requirements of this research. If A_1 is the quantity of acid required to discharge the red color in the cold, and A_2 is the additional amount needed to effect permanent decolorization when boiled, $A_1—A_2$ represents the caustic alkali present.

II.—Formulae for the Interpretation of Results.

A fundamental dynamical theorem of the "action of mass" was stated by Berthelot[3] in 1862, with regard to the formation of ethers,

[1]Zeitsch. anal. Chem. **19**, 457. [2]This Journal, **3**, 55, 232. [3]Ann. chim. phys. [3] **66**, 112

as follows: "The quantity of ether formed at each instant is proportional to the product of the active masses present." Various experimenters have shown that the same law applies to several other reactions that take place in a homogeneous fluid, and the mathematical consequences have already been pretty fully developed.[1] A brief resumé is here given, so far as the formulae are required for the purposes of the present paper.

The fundamental theorem for the action of mass is expressed in the equation

$$\frac{-du}{dt} = auv \tag{I}$$

where u and v are the masses of the two active bodies present at at any moment, the differential coefficient $\frac{-du}{dt}$ is the speed of the action by which u is diminished, and a is some constant which depends upon the intensity of the chemical affinities, the temperature, and other conditions. To apply this formula, it will be convenient to use those units of mass and volume which are generally employed in volumetric analysis; that is, with 1 cc. as a unit of volume, let the chemical equivalent of each substance expressed in milligrams be the unit of mass for that particular substance; thus, the unit of NaOH is 40 mg., that of Na_2CO_3 is 53 mg., etc. If the symbols u and v represent the quantities present in the unit of volume, they express the concentration of the solution with respect to the two bodies, where unity denotes a normal solution, 0.1 denotes a decinormal solution, and so on.

Let u_0, v_0 = the concentration at the beginning of any interval, and u^t, v_t = the concentration at the end of the same; then, since equivalent amounts of the two active bodies are simultaneously rendered inactive by simple metathesis, $v_t - u_t = b$, which is a constant, independent of the interval t.

Hence, $$\frac{-du}{dt} = au(u+b); \quad \frac{-du}{u(u+b)} = adt. \tag{II}$$

When the two substances are present in equivalent amounts, $b = 0$, and

$$\frac{-du}{u^2} = adt. \qquad (2)^2$$

[1] Berthelot, *loc. cit.* J. H. van't Hoff, *loc. cit.* Hood, Phil. Mag. [5] **6**, 371; **8**, 121. Guldberg and Waage, J. pr. Chem. [2] **19**, 69, etc. Muir, Phil. Mag. [5] **8**, 181.

[2] The more general equations are distinguished in this paper by Roman numerals; those which apply only under the restriction that $b = 0$, by Arabic numerals.

By integrating equation II.,

$$l_e\left(\frac{u_t + b}{u_t}\right) = abt + l_e\left(\frac{u_0 + b}{u_0}\right) \tag{III}$$

$$\therefore \quad a = \frac{l_e\left(\frac{u_t + b}{u_t} \cdot \frac{u_0}{u_0 + b}\right)}{bt} = \frac{\log.\left(\frac{u_t + b}{u_t} \cdot \frac{u_0}{u_0 + b}\right)}{0.4343bt} \tag{IV}$$

where l_e represents the Naperian logarithm and log. represents the common logarithm.

Likewise from eq. (2) we find

$$u_t = \frac{u_0}{au_0\, t + 1} \tag{3}$$

$$\therefore \quad a = \frac{u_0 - u_t}{u_0 u_t\, t} \tag{4}$$

It may sometimes be desirable to eliminate the effect of any irregularity during the process of mixing the two substances; for this purpose eq. (4) may take the form

$$a = \frac{u'_0 - u_t}{{}_0'u_t\, t'} \tag{5}$$

where u'_0 = the value of u as determined by the first titration of a series, and the interval, t', is counted from this titration.

When b is very small in comparison with u_0 and u, the formula

$$a = \frac{u_0 - u_t}{u_0 u_t\, t} \cdot \frac{u_0 + u_t}{u_0 + u_t + 2b} \tag{V}$$

gives a close approximation to the correct value.

It may be observed that the curve representing the relation between u and t may vary from an equilateral hyperbola (when $b = 0$) to a logarithmic curve (when $b = \infty$); and eq. (V) nearly expresses the former, if b is very small.

Equation (IV), (4), (5) or (V) (according to the conditions of the experiment) affords a valuable criterion in researches on the speed of chemical action. Where the initial conditions are known, each determination of u, at the end of a measured interval, t, is sufficient to deduce a value for a, which may be called the "coefficient of speed"; and if the reaction is one of simple metathesis, and not affected by any disturbing change of conditions, the theorem requires that a series of observations shall give nearly

agreeing values for a. A disturbing cause,[1] on the other hand, may often be detected by a series of determinations in which the values deduced for a are found to increase or decrease with some regularity.

It is evident that the rate of chemical action in dilute aqueous solution will depend in part upon the rate of diffusion by which the active bodies are continually being brought into contact. Schuhmeister[2] has shown that when the concentration of the haloid salts of potassium is reduced from 0.3 per cent. to 0.1 per cent. the diffusion constant is diminished by nearly 11 per cent. It is probable, therefore, that a more complete investigation of the theory of the action of mass in very dilute solution will require a modification of the above equations, by substituting for a in eq. (I) some function of u and v.

III.—Application of the Theorem and Formulae to Saponification by Sodic Hydrate.

The ethyl acetate used had neutral reaction, but was not constant in its boiling point. Titrated by Wanklyn's[3] method, it neutralized 93.63 per cent., 93.42 per cent. and 94.41 per cent. of the theoretical quantity of alkali. As a mean result, 93.82 per cent. of acetate was found to be present; hence a normal solution would require 93.80 grams to the litre. The impurity had a low boiling point, and seemed to consist chiefly of ethyl oxide. Qualitative tests for water and free alcohol gave negative results. A $\frac{1}{2}$ normal solution was readily prepared by weighing out the required amount of the ether in a $\frac{1}{4}$ litre flask, and filling up to the mark with water; but after a short time bubbles of gas or vapor were seen to separate upon the sides of the burette, perhaps consisting of ethyl oxide, and requiring some watchfulness in measuring.

The acid used was $\frac{1}{8}$ normal, carefully standardized with pure sodic carbonate.

The soda solution was approximately $\frac{1}{8}$ normal.

For 18.85 cc. alkali, $A_1 = 19.22$, $A_2 = 0.17$, $A_1 - A_2 = 19.05$ cc.

" 23.60 " $A_1 = 24.07$, $A_2 = 0.19$, $A_1 - A_2 = 23.88$ cc.

From these determinations (which were made on different days) the caustic alkali is found to be $\frac{1.010}{8}$ normal and $\frac{1.012}{8}$ normal; the mean factor is $\frac{1.011}{8}$. The amount of caustic soda was very

[1] Harcourt and Esson discuss a remarkable case, in which the manganous sulphate formed by the action of $K_2Mn_2O_8$ and H_2SO_4 upon $C_2H_2O_4$ *accelerates* that action.—Chem. Soc. J. **20**, 460.

[2] Wien. Acad. Ber. April 1879, and Beibl. zu Ann. Phys. **3**, 682.

[3] Chem. Soc. J. [2] **5**, 170.

slightly diminished by the short exposure to air in the process of measuring, and by traces of CO_2 in the distilled water added; hence the value of A_2 was also determined after saponification. In the very dilute solutions to be titrated, this was rendered the more difficult from the presence of sodic acetate, which is decomposed on long boiling, and gradually acquires alkaline reaction towards phenol phthalein. The correction for the carbonate is so small, however, that this error will not invalidate the general result obtained in the following series:

Series I. Temperature was 20.5° to 20.6°. A mixture was prepared, consisting of

501 cc. water,
99 " $\frac{1.01}{8}$ normal NaOH, and
25 " $\frac{1}{2}$ " $C_2H_5.O.C_2H_3O$;

making 625 " in all; which was thus a $\frac{1}{50}$ normal solution of alkali and ether; that is, $u_0 = v_0 = 0.02$. 100 cc. were drawn out for each titration. A mean value of 0.35 cc. was assumed for A_2, in each determination of causticity. The observed values of $A_1—A_2$ are compared below with those calculated from the mean value deduced for a. The time is expressed in minutes.

Time.	$A_1—A_2$ Observed.	$A_1—A_2$ Calculated.	Errors.	$a = \frac{u_0—u_t}{u_0\, u_t\, t}$
5	10.24 cc.	10.36	—0.12	5.625
15	6.13	6.07	+ .06	5.37
25	4.32	4.29	.03	5.405
35	3.41	3.32	.09	5.27
55	2.31	2.29	.02	5.385
120	1.10	1.13	— .03	5.645

Mean value of $a = 5.45$

Series II. Temperature was 21.0° to 21.3°. The same quantities were taken as in Series I. $A_2 = 0.35$.

Time.	$A_1—A_2$ Observed.	$A_1—A_2$ Calculated.	Errors.	$a = \frac{u_0—u^t}{u_0\, u_t\, t}$
5	10.15 cc.	10.26	— 0.11	5.765
15	6.06	5.97	+ .09	5.465
25	4.23	4.21	.02	5.57
35	3.29	3.25	.04	5.52
45	2.61	2.65	— .04	5.70

Mean value of $a = 5.60$

The calculated and observed values for $A_1—A_2$ show a pretty fair agreement with the fundamental theorem, and indicate that the process is nearly free rom secondary reactions or other disturbing causes.

If the initial period of action is eliminated by formula (5), the mean results found above are reduced to $a = 5.35$ at 20.5° to 20.6° and $a = 5.50$ at 21.0° to 21.3°; hence the values obtained by making a single titration under the conditions of these series are probably liable to be a little too high. The significance of the values found for a will be readily deduced from eq. I. by making u and v each equal to unity. The "coefficient of speed" then appears as *the number of milligram-equivalents per cc. which* (according to the accepted theory of the action of mass) *would react upon each other in one minute, in a solution kept at normal strength.*

It must be stated, however, that in several series of experiments the calculated value of a was found to diminish steadily instead of being constant, even with the precautions described above; so that further examination may possibly indicate how the fundamental theorem and resulting formulae must be modified, in order to include any necessary correction for variation in the diffusion constant, etc., as already suggested. Circumstances prevented a more thorough investigation, at this time, of some possible causes of variation in the experimental results; and the fundamental theorem is accepted with regard to the reaction studied, as representing a sufficiently close approximation to the truth. Even if the values deduced for a should not have the exact value defined above, they will yet serve for the comparison drawn in the next section.

IV.—Influence of Temperature.

To study the relation between the coefficient of speed and the temperature, I prepared two liters of $\frac{1}{32}$ normal ether solution. For each determination I drew out 100 cc., cooled or warmed it as might be desired, added about 25 cc. of $\frac{1.01}{8}$ normal HNaO, corked tightly, and maintained a nearly constant temperature until the moment arrived for adding the standard oxalic acid. The period of action was made to vary from twenty minutes at low temperatures to four minutes at the highest temperature, in order to secure favorable conditions for accurate measurement, the action being generally arrested when about half the ether had been saponi-

fied. Since 100 cc. of $\frac{1}{32}$ normal ether solution was increased to a volume of 125 cc., the mixture was $\frac{1}{40}$ normal with regard to the ether, or $u_0 = 0.025$. The alkali was added from a full burette, about 10 seconds being required for the desired amount to flow out. Ten minutes were generally allowed before taking the final reading of the burette, that the surface of the somewhat viscous solution might become stationary. The initial quantity of NaOH was carefully estimated from the volume taken in each case, its original strength, and the traces neutralized by CO_2, on flowing into the solution of ether. The values of u_0 and v_0 in no case differed more than two to three per cent., and usually the difference was much less. In the determinations of causticity, a mean value of 0.5 cc. was assumed for A_2 throughout this series. The numerical results obtained, as calculated by eq. (V), are given in the following table, as the "observed" values of a. The mean temperatures are given under t; variations of some tenths of a degree could not be avoided with the appliances used. The "calculated" values of a are obtained by means of various empirical formulae, as explained below.

SERIES III.

t.	a Observed.	a calculated. A.	B.	C.
3.6°C	1.418	1.351	1.585	1.543
5.5	1.680	1.645	1.695	1.684
6.0	1.782	1.728	1.735	1.731
6.6	1.730	1.826	1.788	1.793
7.2	1.920	1.928	1.848	1.861
11.0	2.563	2.623	2.373	2.428
12.4	2.788	2.906	2.630	2.707
12.7	2.875	2.969	2.690	2.768
19.3	4.568	4.567	4.403	4.490
20.0	4.732	4.771	4.630	4.716
20.4	4.779	4.882	4.763	4.848
20.9	4.989	5.031	4.934	5.018
23.6	6.010	5.903	5.933	6.003
27.0	7.243	7.186	7.371	7.414
28.4	8.034	7.786	8.022	8.049
30.4	8.876	8.740	9.013	9.014
32.9	9.868	10.112	10.349	10.310
34.0	10.92	10.79	10.97	10.91
35.0	11.69	11.46	11.56	11.48
37.7	13.41	13.52	13.23	13.09

The several equations given below serve to reproduce the observed values of A, with probable errors for each observation, as follows:

For formula A, probable error $= \pm 0.087$
" " B, " " $= \pm 0.107$
" " C, " " $= \pm 0.112$

The points whose coördinates are t and a, after being platted upon engineer's profile paper, were found by a method of approximation to lie near the curve

$$(7.5 + a)(62.5 - t) = 521.4$$[1]

or

$$a = \frac{521.4}{62.5 - t} - 7.5 \qquad (A)$$

But since it is usual, in similar investigations, to use equations of the form

$$a = A + Bt + Ct^2 + \text{etc.},$$

I selected seven points lying near the smooth curve of the diagram, and by the method of least squares obtained the equation

$$a = 1.55 - 0.022\,t + 0.0088\,t^2 \qquad (B)$$

The coefficient B of the empirical formula can be made equal to zero, without greatly affecting the form of the curve within the range observed. The most probable equation of two constants is

$$a = 1.436 + 0.0082\,t^2 \qquad (C)$$

These constants are deduced from all the observations of Series III., by the method of least squares; but the refinement of assigning a particular weight to each observation was omitted.

The curves represented by these three equations lie quite close together, as shown by the calculated values given in the table. A closer agreement with the observations would have been obtained by an equation of the form

$$a = A + Ct^2 + Dt^3.$$

Each curve becomes rapidly steeper as t is increased. It is impossible at present to determine the precise form of the equation representing the relationship under discussion; for even within the limited range of 34.1° there were special sources of error affecting the two extremes of the series; yet it may be safely assumed that

[1] As stated in my preliminary note, this Journal, **3**, 203.

the increase of speed is approximately as the second power of the temperature[1] as represented in eq. (*C*).

If we try to picture the progress of the reaction in dilute aqueous solution, we realize that the molecules of the two "active" substances are greatly retarded in their chemical interchange by the vastly greater number of "inactive" water molecules. If the water were physically as well as chemically inactive, the chemical change would soon become impossible, because the separated ether and soda molecules could not come within the sphere of each other's influence. It can scarcely be doubted that the speed of chemical action increases with the temperature for a double reason; first, because the *liquid diffusion* is thereby increased by which the chemically active bodies are brought together, and secondly, by the increased *inter-atomic motion* within the reacting molecules, by which their sphere of mutual influence is enlarged. Weber's recent researches[2] on diffusion, as well as the older experiments of Eckhard,[3] show that *the increase in the coefficient of diffusion for dilute solutions is nearly proportional to the first power of the temperature.*

It may also be mentioned in this connection that the electrical conductivity of solutions (if not unusually viscous) is shown by Exner and Goldschmiedt[4] and by Kohlrausch[5] to vary far more nearly with the first power than the second power of the temperature.

To distinguish precisely between the two causes of increased speed of chemical action with higher temperatures, to show how much is due to more rapid diffusion, and how much must be attributed to the strictly chemical causes manifested within the molecules, will of course require more extended and accurate experimental data. It seems evident, however, that the foregoing determinations indicate that *an increase of temperature is accompanied by an increase of atomic motion within the several molecules of the fluid.*

Believing that the work done thus far has chiefly served to prepare the way for more accurate and extended investigation, with promise of fruitful results, I hope to continue this research as soon as circumstances will permit, with the aid of less active saponifiers.

North Bend, Ohio, *July* 25, 1881.

[1] Hood suspected that the action of $KClO_3$ upon $FeSO_4$ varies as the square of the temperature.—Phil. Mag. [5] **6**, 383.

[2] Wied. Ann. Phys. **7**, 469, 536.

[3] Pogg. Ann. **128**, 61.

[4] Wied. Ann. Phys. **4**, 417; **6**, 73.

[5] Wied. Ann. Phys. **6**, 1, 145.

XXIV.—SOME NEW COMPOUNDS OF PLATINUM.

By F. W. Clarke and Mary E. Owens.

The action of potassium cyanate upon the compounds of platinum seems never to have been systematically studied. We have begun an investigation upon the subject, and now present some of our earlier results.

When cold alcoholic solutions of platinum tetrachloride and potassium cyanate are mixed, a pale buff-yellow precipitate is thrown down. If the mixture is heated, this precipitate undergoes partial decomposition, and what is apparently metallic platinum separates out. By filtration, washing with alcohol, and drying at ordinary temperatures over sulphuric acid, the precipitate may be obtained in a stable condition. It is soluble in water, but completely insoluble in alcohol, and its aqueous solution decomposes upon boiling. Analysis gives the following percentages, which agree with the novel formula $K_2PtCl_5(CNO).H_2O$.

	Found.			Theoretical.
Pt	38.41	38.44	38.6	38.19
Cl	34.79	5.19	34.74	34.77
K_2	15.08	14.53	14.67	15.28
C	2.27	...	...	2.35
H_2O	3.76	3.22	...	3.52

For want of sufficient material, nitrogen was not estimated. The presence of the cyanic molecule in the compound is, however, unquestionable.

By the action of potassium cyanate upon the green salt of Magnus, $PtN_2H_6C_2$, new compounds are formed, apparently of great complexity. The Magnus salt was prepared by the addition of a solution of potassium chloroplatinite to aqueous ammonia. A pure product is thus almost immediately formed, whereas the methods hitherto laid down for the preparation of this body gave us very unsatisfactory results. The Magnus salt dissolves readily in a hot aqueous solution of the cyanate, yielding a dark brown solution; which, concentrated over the water-bath to its crystallizing point, deposits pale yellow needles. From the mother liquor, beautiful clusters of brown needles were obtained. The yellow salt contained platinum, potassium, ammonia, water, and

carbon; the platinum amounting to 43.93 per cent. In the brown crystals, ammonia, platinum, and chlorine were found. Both salts are to be systematically investigated.

One other new salt was incidentally obtained by us. The well known potassium sulphocyanoplatinate is prepared by the action of potassium sulphocyanate upon the chloroplatinate. Happening to have a quantity of the strychnia chloroplatinate on hand, we dissolved it in potassium sulphocyanate. The blood-red solution, which was obtained after short boiling, deposited on cooling a brilliant red crystalline precipitate. This proved to be the strychnia salt analogous to the potassium sulphocyanoplatinate, and gave percentages of platinum and sulphur agreeing with the formula $2(C_{21}H_{22}N_2O_2)H_2PtCy_6S_6$.

	Found.	Theoret cal.
Pt	14.12	14.49
S	13.76	14.01

Doubtless other sulphocyanoplatinates of alkaloids may be easily obtained.

The investigation of the products resulting from the action of cyanates upon platinamines is to be followed up at an early day. The whole subject of the reactions between cyanates and salts of the various metallamines and metallammoniums bids fair to yield results of considerable interest.

XXV.—ON SOME SALTS OF CHROMIUM AND MERCURY.

BY F. W. CLARKE AND DAVID STERN.

The double salts which mercuric chloride and mercuric cyanide form with certain alkaline chromates have long been known. The following have been described.

1. $(NH_4)_2Cr_2O_7.HgCl_2.H_2O$ Darby, Richmond and Abel.
2. $3(NH_4)_2Cr_2O_7.HgCl_2$ Richmond and Abel.
3. $K_2Cr_2O_7.HgCl_2$ Millon. Darby.
4. $K_2CrO_4.2HgCl_2$ Darby.
5. $K_2CrO_4.2HgCy_2$ Poggiale. Caillot and Podevin.
6. $Ag_2Cr_2O_7.2HgCy_2$. Darby.

These salts we have subjected to a reëxamination, and we have sought to prepare others of the same series.

The first of the foregoing compounds was our chief object of study. Our results concerning the others may be stated briefly. Salts numbered 3 and 4 we prepared, but found them difficult to purify. To number 5, Darby and Rammelsberg both assign the formula $2K_2CrO_4.3HgCy_2$. This formula requires 9.09 per cent. of chromium, while the one given above corresponds to 7.45 per cent. We found 7.62 per cent., thus confirming the simpler formula. The salt numbered 6 we found easy to prepare, and we verified its composition. We tried also to obtain a corresponding salt containing thallium in place of silver, but only thallium dichromate was deposited. We also attempted to produce double salts of mercuric cyanide with ammonium chromate, ammonium dichromate, and potassium dichromate, and of mercuric chloride with ammonium chromate; but in none of these experiments were we successful.

The salt numbered 1, and given by Richmond and Abel the formula $(NH_4)_2Cr_2O_7.HgCl_2.H_2O$, is easily prepared. The salts represented in it are dissolved together in equivalent proportions, and from the concentrated solution the double compound is deposited in large, showy crystals. As obtained by us, however, it was anhydrous. As formulated by Richmond and Abel, it should contain 3.33 per cent. of water; but, as obtained by us, it lost no weight even after long heating at 150°. An estimation of chromium gave us 19.80 per cent. The theoretical percentage for an anhydrous salt is 19.88; for a monohydrated compound, 19.22.

From the mother liquor of the foregoing compound Richmond and Abel obtained the salt which we have numbered 2. This body we did not obtain. Various attempts were made to prepare it, but all were unsuccessful. Several crops of the original salt were deposited in succession, and finally some orange-red laminae were secured which were neither ammonium dichromate nor either of the double salts above referred to. They were, however, contaminated with mercuric chloride, and were not in sufficient quantity for purification and complete analysis. To the mother liquor from them ammonia was added. A heavy dirty yellow precipitate was at first formed, which redissolved in an excess of the precipitant. The solution thus obtained deposited dark clove-brown granular crystals, also in quantity insufficient for thorough analysis. They

were insoluble in cold water, but boiling water decomposed them, with separation of a yellow basic chromate of mercury. At 150° the crystals lost 1.68 per cent. of their weight, and at 200° 16.66 per cent. 17.04 per cent. of chromium, 8.89 of ammonia, and 43.70 of mercury were found in them, but no chlorine. From this meagre evidence we can deduce no probable formula; but we suspect the body to be a double salt of an ammonium chromate, with a chromate of one of the mercurammonium bases.

Upon adding a caustic alkali to a solution of the salt $(NH_4)_2Cr_2O_7.HgCl_2$, a yellow precipitate was thrown down, which proved to be a basic chromate of mercury. From hot solutions precipitates were formed of variable composition; but from cold solutions a compound was deposited consisting definitely of the salt $7HgO.2CrO_3$. Our analytical results were as follows, in percentages:

	Ammonia ppt.	Soda ppt.		Theoretical.
Cr	6.08	6.09	6.14	6.07
Hg	80.74	81.41	...	81.77

The same compound was partially studied in this laboratory two years ago by Miss Helena Stallo, but her results were not published. She obtained the following percentages of chromium:

	NH_4OH ppt.	NaOH ppt.	KOH ppt.
Cr	6.09	5.96	6.07

These figures are interesting, inasmuch as the same compound was prepared by a different process by Geuther,[1] whose results were afterwards discredited by Freese.[2] According to the latter chemist there is probably but one basic mercuric chromate, viz., the tribasic compound $3HgO.CrO_3$. Our results confirm Geuther's, and from another line of investigation. The following equation represents the formation of the salt:

$$7(Am_2Cr_2O_7.HgCl_2)+24NaOH$$
$$=12Na_2CrO_4+14AmCl+7HgO.2CrO_3+12H_2O.$$

The addition of a solution of borax to a solution of the salt $Am_2Cr_2O_7.HgCl_2$ also produces a yellow precipitate. This product agrees fairly with the formula $4HgO.CrO_3$, as the subjoined figures show:

	Found.	Theoretical.
Cr	5.10	5.38
Hg	82.34	82.88

[1]Ann. Chem. Pharm. **106**, 244. [2]Poggend. Annal. **140**, 76.

The filtrate from this precipitate, upon concentration, gave white scaly crystals, which proved upon analysis to be boric acid. Hence, the following equation is probable:

$$4(Am_2Cr_2O_7.HgCl_2)+7Na_2B_4O_7$$
$$=7Na_2CrO_4+8AmCl+4HgO.CrO_3+14B_2O_3.$$

If, instead of borax, hydro-disodic phosphate be used for a precipitant, still another basic chromate is thrown down. It agrees approximately with the formula, $6HgO.CrO_3$.

	Found.		Theoretical.
Cr	4.07	4.04	3.79
Hg	86.43	...	85.96

This corresponds to the subjoined equation,—

$$6(Am_2Cr_2O_7.HgCl_2)+11Na_2HPO_4$$
$$=11Na_2CrO_4+12AmCl+6HgO.CrO_3+11HPO_3.$$

The last term in the equation was not verified, but it is suggested by the actual formation of boric acid in the previous case.

In conclusion, our results establish the existence of the basic chromate, $7HgO.2CrO_3$, and render the existence of two other basic chromates of mercury highly probable. All three are thrown down definitely from cold solutions, and all are more or less changed by boiling.

THE ELECTROLYTIC DETERMINATION OF COPPER AND THE FORMATION AND COMPOSITION OF SO-CALLED ALLOTROPIC COPPER.[1]

By J. B. Mackintosh.

The quantitative determination of copper by means of electrodeposition offers so many advantages, that it is to be preferred, when properly executed, to all other methods for ease and accuracy. The object of the present paper is to give the results of a number

[1] Read at the Virginia meeting of the American Institute of Mining Engineers.

of experiments made during the past few months, and to indicate some sources of error which must be avoided in order to attain the necessary accuracy.

In 1867, C. Luckow, in competition for a prize offered by the directors of the Mansfield Copper Works, submitted the following process for the estimation of copper, and received, not indeed the prize, but an honorable mention for the simplicity, cheapness, and elegance of his process. He directs that the copper and the accompanying metals be obtained in the form of nitrates in solution in dilute nitric acid containing not more than 0.100 gram of the pure acid in each cubic centimeter; to this solution is added a few drops of a solution of an organic acid, such as tartaric or oxalic, and the copper is then precipitated on platinum in the usual manner. It is claimed that the copper is obtained in beautiful reguline form, while zinc, iron, and nickel are not precipitated at all.

In adapting this method to the analysis of copper alloys, I dissolved the alloy in nitric acid, evaporated the solution to dryness to get rid of the excess of acid, dissolved the residue in water with the addition of a few drops of nitric acid, to dissolve the basic nitrate of copper formed, and to this solution added four or five drops of a concentrated solution of citric acid. This solution was then precipitated in a platinum dish with a current from two Bunsen cells of about one quart capacity. In precipitating several samples at once I have it arranged so that the whole current traverses the row of dishes, the negative pole of each set being connected with the positive pole of the next succeeding one. In this case, if n be the number of dishes, then $n+1$ is the number of battery cells of that size used.

Some of the results obtained by this method, and on duplicate portions by precipitation from sulphuric acid solution, are as follows:

	Sulphuric Acid.	Nitric+Citric Acid.	Error.
1 gram pig copper	98.00	99.42	+1.42
" "	99.80	101.22	+1.42
" "	98.92	100.41	+1.49
" "	98.72	100.27	+1.55
" "	99.60	100.45	+0.85
1 gram brass	65.83	66.93	+1.10
" "	65.83	66.58	+0.75

In only one case was a smaller percentage obtained by the use of this method, and in that case the precipitation of the copper was not complete. In many cases, also, in which the amount of error was less than one per cent., small quantities of copper escaped precipitation and were afterwards found in the solution.

The metallic precipitate thus produced is of a much lighter color than ordinary copper from the electrolysis of the sulphate solution, but it is, as Luckow says, deposited in beautiful reguline form, which, however, hardly compensates for the error of perhaps one per cent. or more which we see is, as a general rule, the case.

Moreover, if the current is strong, after all the copper has been thrown down, zinc will be deposited on the surface of the copper, as a dark coating, which may be recognized as such by dissolving in dilute sulphuric acid and applying appropriate tests.

In the presence of the organic acid the formation of peroxide of lead on the positive pole is hindered, and in its absence it is very difficult to precipitate the whole of the copper from the solution.

In order to obtain sufficient material for analysis, to ascertain the cause of the excess in weight, the precipitation of the copper was made on a piece of platinum foil. On attempting to strip the deposit from the foil, I found that it was extremely brittle and scaled off easily; so brittle, indeed, that it could be reduced to an impalpable powder in an agate mortar with very little trouble. This agrees exactly with the description of the allotropic copper of M. P. Schützenberger, which was published in *Comptes Rendus*, vol. 86, part 2. M. Schützenberger obtained the material he describes by the electrolysis of a ten per cent. solution of the neutral acetate of copper. He found that the product contained from five to ten per cent. of suboxide of copper. In the material which I prepared from the nitric and citric acid solution I did not find *any* suboxide of copper; on the other hand, both carbon and hydrogen have been detected and estimated. These latter were determined by combustion of the finely divided sample in oxygen; the method used to estimate the suboxide of copper was that of Hampe.[1] However, oxygen is present, though, as this test shows, not as cuprous oxide.

The results of the analyses of several samples, prepared at different times, are given below. The determinations were all made on the amount of one grain:

[1] Zeitschrift für analytische Chemie, 1878, 127.

	a	b	c	d	e	f	g	h
Carbonic acid...............	.0273	.0316	.0350	.0344	.0322	.0324	.0346	.0283
Equivalent to Carbon.......	.00744	.00862	.00954	.00938	.0088	.0088	.0094	.00771
Water................	.0094	.0108	.0089	.0094	.0054	.0045	.0074	.0054
Equivalent to hydrogen.....	.00104	.00120	.00100	.00104	.0006	.0005	.00082	.0006
Ratio of carbon to hydrogen.	7.15	7.18	9.54	9.0	14.6	17.6	11.46	12.42
Copper....................			.9683	.9687				
Total.....................			.97884	.97912				

The results which are bracketed are from duplicate analyses. These samples were all prepared from the nitric and citric acid solution. *a*, *b*, and *c d* were prepared simultaneously, the solution of *b* containing a little more citric acid than that of *a*, and *c d* more than either. The samples *e*, *f*, *g*, and *h* were heated to about 100° C. for fifteen minutes before being introduced into the combustion tube, and the samples *c*, *d*, *e*, and *f* were the same. The results given under *h* are low, probably due to imperfect oxidation.

It will be seen that there is a deficiency of .02116 and .02088 respectively in the total of the duplicate analyses *c* and *d*. The precaution was taken in one case, of passing the products of the combustion over a red hot layer of oxide of copper, to make sure that no hydrocarbon was distilled out by the gradually increasing heat and so escaped oxidation. The results in this case, however, differed in no material manner from those already obtained. We must, therefore, conclude that this deficiency must consist either of *oxygen* or *nitrogen*, or of a mixture of both. I have already mentioned that there is no oxygen in the form of cuprous oxide present, so that it must, if present, be combined in some other form. The following synthetical experiments seemed to indicate that *nitrogen* was also an essential constituent.

These experiments were conducted as follows: Solutions were prepared of nitrate and of sulphate of copper; to these solutions were added respectively, citric acid, tartaric acid, and alcohol. All three of the solutions of the nitrate furnished the brittle deposit,

while all three of the sulphate solutions gave a tough deposit of apparently ordinary electrotype copper. The amount of copper was determined in 1.0008 gram of the precipitate from the sulphate solution containing alcohol, and found to be 0.9991. This difference is probably due to impurities in the copper, which was prepared in the first place from the commercial sulphate, which contained lead and other impurities.

During the electrolysis of the nitrate solutions containing citric acid, a very strong odor of hydrocyanic acid was perceptible.

If an insufficient amount of organic matter be added, the precipitated copper obtained is not brittle, but it nevertheless contains carbon and hydrogen and gives a total result less than 100 per cent. This is due to admixture of ordinary copper. It is not possible to divide such a precipitate sufficiently finely to ensure perfect oxidation.

The amount of nitrogen present in the nitric-citric precipitated copper, was determined by heating the finely pulverized sample in a vacuum and collecting the gases evolved. The products thus obtained were hydrogen, carbonic acid, and nitrogen. When heated in an atmosphere of oxygen, insufficient to completely oxidize the copper, the products were water, carbonic acid, and nitrogen. Although in this case it was probable that an excess of oxygen would be present, yet the analytical results showed the absence of that gas in any appreciable quantity.

The volumes given are those of the dry gas at 0° C. and 760 mm.

	1 gram heated *in vacuo.*	½ gram in Oxygen.	1.15 gram in Oxygen.
Gas obtained,	9.95 cc.	8.23 cc.	17.52 cc.
CO_2 absorbed by KOH,	4.72 "	7.35 "	15.70 "
Gas not CO_2,	5.23 "	0.88	1.82 "
Ogygen added,	7.77 "		
	13.00 "		
Volume after explosion,	7.44 "		
Loss—Water,	5.56 "		
No CO_2 formed: *Hydrogen*,	3.71 "		
Residue: *Nitrogen*,	1.52 "		

These residues treated with moist phosphorus to absorb oxygen, and then with KOH, did not change, proving the absence of oxygen.

The circumstances of formation were such as to preclude the existence of hydrogen, therefore these residues must be nitrogen.

The percentage results in the foregoing three cases are respectively for nitrogen: 0.191, 0.221, 0.199; and in the two last for carbon: 0.792, 0.736. The ratio of $\frac{C}{N}$ being 3.6 and 3.7.

One sample of the product, made with tartaric acid, weighing two grams, was also analyzed for nitrogen, and one cubic centimeter of dry nitrogen at 0° C. and 760 mm. obtained. It is difficult when working on such small quantities of gas to obtain very accurate results.

Some of the allotropic copper prepared from the chemically pure acetate according to M. Schützenberger's directions, and which therefore could not contain nitrogen, and also some prepared from an acetate of copper containing nitrate of soda, were compared and analyzed. The material thus obtained was apparently the same in both cases, and differed considerably in some of its properties from the nitric-citric acid solution precipitate. In appearance, brittleness, and composition there was no essential difference, but it was very unstable and liable to oxidize, in fact it was not possible to preserve it of constant composition in the air, while the nitric-citric precipitate can be preserved indefinitely without change.

Two samples of 1.0014 and 1.0004 grams respectively were weighed out. The first was heated for about fifteen minutes to 100° C. in an air-bath; on cooling and weighing it had gained 0.0215 gram. The second sample was exposed to the air at the ordinary temperature for two hours and three-quarters, at the end of that time it had gained 0.0225 gram; it was then heated to 100° C. for fifteen minutes, when it lost 0.0020 gram, giving a net gain of 0.0205 gram.

The amounts of carbon and hydrogen were determined in the second sample of the material from the acetate solution containing nitrate of soda, and in two samples from the chemically pure acetate preparation.

	$Cu(C_2H_3O_2)_2$ $+NaNO_3$	$Cu(C_2H_3O_2)_2$	
Amount taken,	1.004 gram[1]	1 gram	1 gram
CO_2 found	.0145	.0175	.0154
Equivalent to C	.00395	.00477	.0042
H_2O found	.0081	.0092	.0081
Equivalent to H	.0009	.00102	.0009
Ratio, C : H	4.4	4.676	4.666

The cause of the rapid oxidation of these samples seems to be that the deposit is very porous, while that from nitric solutions is very dense.

[1] Oxidized by exposure to air and heating in air-bath before combustion.

M. Schützenberger mentions that he had at one time a considerable quantity of this allotropic copper (*sic*) reduced to powder and dried in a vacuum, which at the moment when air was admitted to it was transformed to ordinary copper, attended by a considerable evolution of heat. The amount of oxygen he found was not altered by this occurrence.

To account for this phenomenon he frames the theory that the allotropic copper corresponds to cuprous copper, and that the molecular change to cupric copper is accompanied by the development of heat. But we can easily see how liable to spontaneous oxidation a large quantity of such finely divided material would be when it contains both carbon and hydrogen in a weak state of combination, and it is unnecessary to suppose the existence of another form of metallic copper to account for the phenomena noticed.

The practical conclusions to be drawn from these results are, that some organic matters, and in all probability all, in the presence of nitric acid in the copper solution undergoing electrolysis, cause erroneous results; that from a nitric acid solution, with no organic matter, it is extremely difficult to separate all the copper; and that the old method of electrolysis from the sulphate is the best.

HOBOKEN, N. J.

REVIEWS AND REPORTS.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

GASTRIC DIGESTION AND THE PRODUCTS FORMED.

Forms in which Pepsin occurs.—Recent facts lead to the opinion that the ferment pepsin contained in the mucous membrane of the stomach exists there in two distinct forms: the one readily soluble, the other slowly and with difficulty. Thus Brücke[1] remarks that a mucous membrane which has been thoroughly extracted with very dilute hydrochloric acid still yields pepsin again and again at each fresh extraction. Likewise Schiff[2] has found that a hydrochloric acid infusion of the mucous membrane when allowed to stand some weeks, grows richer and richer in pepsin, especially when a large quantity of fluid has been employed. Again, the investigations of

[1] Vorlesungen, 1 Auf. 287, 1874.

[2] Arch. d. sc. phys. et nat. 1877.

Ebstein and Grützner[1] have shown conclusively that that portion of the pepsin difficultly soluble does not exist free in the glands, but is united to another substance, probably an albuminate, a pepsinogen compound which Schiff has named *propepsin.*

The following are a few of the facts which tend to further support the idea of a pepsinogen substance.[2] If a portion of dried and finely divided mucous membrane (from cardiac or pyloric region) is laid in glycerin, a glycerin extract is obtained which contains less pepsin than when the glycerin extraction is preceded by a preliminary treatment with 1 per cent. sodium chloride solution or .2 per cent. hydrochloric acid. The reason of this, as Heidenhain says, is not that the glycerin possesses only a limited solubility for pepsin, for the content of pepsin increases with the quantity of mucous membrane employed, but that only one part of the pepsin is originally soluble in glycerin, while the other is rendered soluble by the action of sodium chloride or hydrochloric acid, both of which presumably cause the pepsin to split off from the body with which it was originally combined; the salt less, the acid more completely. Again, if an aqueous solution of the mucous membrane is evaporated to dryness at 40° C., a residue is obtained which is completely soluble in glycerin. This solution, however, is poorer in pepsin than a solution prepared by dissolving the residue in an equal quantity of dilute hydrochloric acid. It is therefore obvious that the residue left by the evaporation of the aqueous extract contains besides free pepsin a substance which yields pepsin or from which pepsin can be liberated, not however by simple solution in glycerin, but by the action of a very dilute hydrochloric acid. According to Schiff the breaking up of the pepsinogen substance is hindered by a solution of sodium carbonate. Doubtless pepsinogen is an intermediate product in the metamorphosis of the protoplasm of the secreting cell. Being difficultly soluble it may serve the purpose of a reserve fund, from which at any time pepsin can be liberated by the acid of the gastric juice.

Place where Pepsin occurs.—In 1839 Wassmann made the discovery that the glands of the pyloric portion of the stomach of swine differed from the glands of the cardiac region, and since that time until recently the seat of the pepsin formation was supposed to be wholly in the glands of the cardiac portion of the stomach. In 1870–1874 Ebstein and Grützner[3] proved conclusively the presence of pepsin in the pyloric membrane, and from its constant presence they concluded that the glands of the pyloric possessed, in common with the glands of the cardiac, the function of secreting pepsin. Before this, Wassmann and other physiologists had detected pepsin in the pyloric membrane, but they in common with von Wittich and others held that it was present there by infiltration from the cardiac, and in support of this theory Wassmann claimed

[1] Arch. f. d. ges. Physiol. 8, 122, 1874.
[2] Heidenhain in Hermann's Handbuch d. Physiologie, Band 5, 1 Theil. 129.
[3] Arch. f. d. ges. Physiol. 3, 565, 1870. Ibid. 6, 1, 1872; Ibid. 8, 122 and 617, 1874.

that the membrane of the pyloric could be freed entirely from its content of pepsin by repeated washing with water. Friedinger[1] however was not able to remove the pepsin from the pyloric membrane even by 24 hours' washing in running water. About the same time Fick[2] found by artificial digestions with different portions of the stomach mucosa, that the mucous membrane of the pyloric region possessed about one-half the digestive power of the mucous membrane from the cardiac. In 1879 Langendorff[3] made the observation that the *port. pylorica* in an ox embryo contained pepsin, and this at a stage of development when the stomach itself contained an alkaline fluid perfectly free from pepsin, thus showing without a shadow of doubt that the ferment may be formed in the pyloric membrane.

Finally, Klemensiewicz,[4] and later, Heidenhain,[5] by examining the secretion from the isolated pyloric portion of the stomach, proved conclusively the presence of pepsin, while at the same time Heidenhain, more successful in his method of experimentation, succeeded in obtaining from his artificially prepared "pylorous blind sack" an alkaline secretion rich in pepsin for a period of five months, thus establishing on a firm basis the theory of a pepsin formation in the pyloric. Within the last ten years, observations have been multiplied which show a widespread distribution of pepsin, or at least a pepsin-like substance, in animal tissues and fluids. As far back as 1861 Brücke[6] found in urine and in muscle substance, traces of a body which with properly diluted HCl would dissolve fibrin. More recently Kühne[7] has found a similar substance in the mucous membrane of the intestines from dogs and swine, in intestinal juice, in lymphe, dog's blood, brain, and in the lungs, while Munk[8] has found it in human mixed saliva. Naturally the quantities found are exceedingly minute, but still in sufficient amount to identify the substance as a body similar to pepsin in its most important property of dissolving and digesting fibrin. Recent investigations of Krukenberg[9] have likewise shown a widespread distribution of both pepsin and trypsin-like ferments among many invertebrates; thus the secretion from the liver of various crustaceans such as *Homarus vulgaris* showed strong digestive action on fibrin in both acid and alkaline solutions. The same investigator also found a peptic ferment present in the yolk from hen's eggs.

Origin of the Pepsin and free Acid in the Stomach.—In the cardiac glands of the stomach the "Belegzellen" or ovoid cells are supposed to produce the acid, while the "Hauptzellen" or central cells produce the pepsin of gastric juice. The great similarity of

[1] Sitzgsber. d. Wien. Acad. **64**, 5.
[2] Würzburger Vehr. N. F. **2**, 61.
[3] Arch. f. Anat. u. Physiol. 1879, 102.
[4] Sitzgsber. d. Wiener Acad. **3**, Abth. 1875.
[5] Arch. f. d. ges. Physiol. **18**, 169. Ibid. **19**, 154.
[6] Sitzgsber. d. Wiener Acad. Math-naturwiss. Cl. **43**, 618.
[7] Verh. d. naturhist-med. Ver. zu Heidelberg, **2**, 1.
[8] Verh. d. Physiol. Ges. zu Berlin 1876, 24th Nov.
[9] Untersuchungen aus Physiolog. Institute, Heidelberg, **2**, 261–273.

the central cells of the cardiac with the cells of the pyloric was commented on long ago by Ebstein, and later when Heidenhain discovered the formation of pepsin by the pyloric cells he was struck with the similarity of the two, and immediately advanced the theory of a like function for the two kinds of cells. This theory was based particularly on the fact[1] that if a small piece of freshly isolated cardiac gland is placed in a drop of dilute HCl under the microscope and heated to 40° C., the central cells quickly break up and are soon almost entirely dissolved, excepting the shrunken up nucleus. The ovoid cells, however, simply appear swollen and more transparent. Naturally under the above circumstances those cells which contain the ferment will dissolve most rapidly, and it was on this fact that the theory of a pepsin formation in the central cells was originally founded. Again, Heidenhain[2] found that a hydrochloric acid infusion of the lower half of the cardiac glands, in which the proportion of central cells to ovoid cells is greater than in the upper half, was possessed of far greater digestive power than an infusion of the upper half of the glands. Among many other facts which point to the same conclusion we may mention the observations of Sewall,[3] who found in studying the development of the cardiac glands in the embryo of sheep, that the ovoid cells appeared first, and then later the central cells, while the presence of pepsin in the mucous membrane could be detected first, only on the appearance of the latter cells. As is now well known the central cells of the cardiac and the cells of the pylorus differ somewhat both in chemical composition and in form, in the hunger period, from that which they possess in the period of digestion. Thus in the condition of hunger the central cells of the cardiac in an alcohol preparation, examined in glycerin are seen to be large, transparent, and with the exception of the nucleus, very faintly or not at all colored by carmine or aniline blue, while at the end of digestion the cells are very much contracted, turbid with small particles, and capable of being thoroughly stained with carmine. Presumably then the material from which the pepsin or its antecedent propepsin is formed in the central cells of the cardiac or the cells of the pylorus is the albuminous matter of the protoplasm. Thus, if the cells have taken up considerable albuminous matter, or in other words are rich in protoplasm, as in the 8th or 10th hour of digestion, then the cells in an alcohol preparation are very turbid and take on a deep color with carmine, while during the hunger period the albuminous protoplasm is in great part gradually changed into the ferment or the pepsinogen antecedent, when the cells then become clearer and refuse to hold the coloring matter. In the words of Heidenhain, "when food is taken the secretory activity of the stomach commences, by means of which two processes standing to each other in the closest relationship, proceed

[1] See Heidenhain's description in Arch. f. microsc. Anat. **6**, 400.
[2] *Loc. cit.*
[3] Jour. of Physiol. **1**, 320.

hand in hand: the conversion of the pepsinogen substance into pepsin and the secretion of the latter on the one hand, the taking up of new albuminates, and thereby increasing the amount of protoplasm for the purpose of forming new ferment, on the other."

The formation of acid in the stomach is to be looked for wholly, without question, in the cardiac portion, and the cells which secrete it are undoubtedly the large ovoid cells. The acidity of gastric juice was ascribed by Prout to free hydrochloric acid in 1824. Later many investigators denied the presence of free HCl, and in 1840–1850 many prominent authorities, as Lehmann, Lassaigne and others, looked upon lactic acid as the principal acid of gastric juice, and Lehmann in particular accounted for the presence of free HCl in the last portions of the distillation fluid, obtained in distilling gastric juice, by the decomposition of calcium chloride by concentrated lactic acid. Later Lehmann succeeded in obtaining from the concentrated gastric juice of 20 dogs free lactic acid in sufficient quantity to form a crystalline salt for analysis. Blondlot believed that the acidity of gastric juice was due to acid calcium phosphate, and he finally adopted the view which at one time was common, that NaCl was decomposed in the walls of the stomach into NaOH and HCl, the acid giving with the calcium phosphate of blood an acid phosphate, together with a trace of free HCl and H_3PO_4, to which latter fact was due the solvent action of gastric juice on calcium carbonate; a fact which had long been quoted as proof of the presence of free acid. To the work of Carl Schmidt[1] however is due a true understanding of the acidity of gastric juice; he found as a result of 18 analyses that the pure gastric juice of carnivorous animals contained only free HCl, and no trace of lactic or acetic acid, while the juice of herbivorous animals contained besides HCl small quantities of lactic acid, which, however, had its origin probably in the starchy constituents of food. Schmidt's conclusions have never been overthrown, and there is no doubt that the principal acid of gastric juice is HCl. The undoubted occasional presence of various organic acids affords no evidence of incorrectness in the above statement, as they would undoubtedly be liberated from their various combinations by the more powerful hydrochloric acid. It has been recently suggested by Richet[2] that the HCl does not exist in a completely free condition, and he quotes several facts which lead him to this view; the most important of which is that gastric juice does not invert cane sugar, while HCl of the same strength does. This statement, which has been extensively circulated, is without doubt incorrect, for Lenssen[3] has distinctly proved that the formation of glucose from saccharose is a delicate test for the presence of free acid, and that the quantity of sugar formed is a measure of the acidity. The strong mineral acids form much more reducible sugar in the same time

[1] Bidder and Schmidt, Verdauungssäfte 40–50.
[2] Jahresbericht d. Thierchemie, **8**, 239.
[3] Jour. f. prakt. Chemie, **85**, 321. Also Zeitschrift f. analyt. Chem. **14**, 306.

than the organic acids, and act very energetically even in the smallest quantities and at the ordinary temperature. Likewise Szabo[1] has shown that the inverting action of human gastric juice on cane sugar approximates much more closely in its intensity to HCl than to lactic acid, this being very apparent when the three are tested side by side. Richet[2] however considers that the acid of gastric juice is a combination of HCl with leucin, and that this latter body modifies the action of the acid. Still more recently Reinhard v. d. Velden[3] has communicated the results of experiments with human gastric juice which are so decisive as to convince him that HCl is not the primary free acid. He found in a large number of cases that gastric juice obtained by means of a stomach-pump from human stomachs during the first period of digestion, contained no free acid, although the juice was strongly acid. Edinger[4] likewise failed to find any free acid in the acid gastric juice of frogs. After a time, however, free HCl can be detected in the human gastric juice, the length of time varying from ¾ to 2 hours, being apparently dependent upon the kind of food taken.

Many theories have been devised to explain the formation of free HCl in the stomach. Heidenhain is of the opinion that the chloride of the blood is the material from which the HCl is formed, the separation taking place in the stomach glands. Thus, according to his view, the chloride passes into the mucous membrane by diffusion, for Grützner found it present there in quantities sufficient to be detected. He likewise found that the mucous membrane under those conditions in which it was richest in pepsin, contained a much larger quantity of chloride than when by vigorous secretion the content of pepsin had been diminished. Thus Heidenhain is of the opinion that it is the function of the secreting membrane to decompose the chlorides obtained from the blood in order to form HCl for the purposes of digestion; this particular secretory process being presumably the main function of the large ovoid cells. According to his views also the decomposition of the chloride does not at once take place, but an organic acid is first formed which causes the HCl to separate from the alkali. This view is based on Brücke's statement that the substance of the stomach, by digestion in a warm place, develops an organic acid, presumably lactic. Then, too, Maly,[5] as well as others, has furnished direct proof of the possibility of the decomposition of chlorides by lactic acid, for he found that a mixture of sodium chloride and dilute lactic acid to which considerable water had been added, gave in a short time free HCl.

The mother substances from which the acid gastric juice must originally be formed are the alkaline lymphe and blood, and in order to understand the formation of an acid secretion from such a source Buchheim[6] has suggested the possibility of the alkali salts of blood

[1] Jahresber. d. Thierchemie, 7, 267.
[2] *Loc. cit.*
[3] Zeitschrift f. Physiolog. Chemie 3, 205.
[4] Arch. f. microscop. Anat. 17, 198.
[5] Ann. d. Chemie, 173, 228.
[6] Pflüger's Archiv. 12, 326.

behaving to albumin in the same manner as the salts of the heavy metals; thus when albumin is treated with $CuSO_4$, two new compounds are formed, a copper-albumin compound and a sulphuric acid-albumin compound. In an analogous manner sodium-albumin and hydrochloric acid-albumin might originate in the blood, the latter compound undergoing disassociation in the ovoid cells of the stomach. Recently Maly[1] has undertaken to explain the formation of HCl by a totally different method. It has long been known that a mixture of NaH_2PO_4 and NaCl or $CaCl_2$ gives an acid reaction with methylanilin violet, also that such a mixture in water yields by diffusion free HCl. It therefore seems probable that NaH_2PO_4 partially decomposes the chloride, acting towards it like a free acid. It is also a well-known fact that the ordinary disodium phosphate Na_2HPO_4 is changed into the monophosphate by the action of CO_2. Now, according to Maly, all the conditions are favorable for such a change as this to take place in the blood. In blood, both NaCl and Na_2HPO_4 are present, and in the presence of an excess of CO_2, NaH_2PO_4 is also to be found. By the reaction of these bodies small quantities of free HCl are formed, and then owing to its high rate of diffusion the free acid at once passes by osmosis into the glands of the stomach, thus making of these glands a simple diffusion apparatus instead of a secretory one. Again, Pribram[2] and others have called attention to the peculiar action of alkaline disodium phosphate upon calcium chloride, which also appears to be present in the serum of blood. The precipitate produced by the union of these two substances is not exactly $CaHPO_4$, but is richer in calcium, being probably a mixture of di- with some triphosphate, a small quantity of HCl being liberated, which can readily be detected in the filtrate by methylanilin violet. The change which may take place in the above reaction can be expressed as follows:

$$3CaCl_2+2Na_2HPO_4=Ca_3(PO_4)_2+4NaCl+2HCl.$$

That such a change as this actually does take place in the blood is of course wholly hypothetical.

R. H. Chittenden.

(To be continued.)

Report on Analytical Chemistry.

(Continued from p. 231.)

Oxygen.—*Absorption by pyrogallol in alkaline solution.*—Th. Weyl and X. Zeitler.[3] The object of the investigation was to determine the dependence of this absorption upon the quantity of pyrogallol and the concentration of the caustic potassa. The

[1] Zeitschrift f. Physiolog. Chemie, **1**, 174.
[2] Jahresber. d. Thierchemie, **1**, 107. Also **3**, 109.
[3] Liebig's Annalen, **205**, 255.

method of experimenting consisted in passing a carefully measured volume of air through an alkaline solution of pyrogallol, and in determining the unabsorbed oxygen by the method of Schützenberger. The best results were obtained by dissolving 0.25 gram of pyrogallol in 10 cc. of caustic potassa having a specific gravity of 1.05. In this solution the absorption of oxygen was nearly complete.

Volumetric solution for the determination of superoxides and oxidizing substances.—A. Terreil.[1] The solution is prepared by dissolving 100 grams of ferrous sulphate in 500 cc. of water, adding 200 grams of concentrated sulphuric acid and diluting to 1000 cc. After standardizing with permanganate of potassium, from 0.2 to 0.3 gram of the substance (very finely pulverized) is treated with from 30 to 50 cc. of the solution, and warmed if necessary. The excess of ferrous sulphate is then determined by means of permanganate of potassium. In this way the superoxides of hydrogen, barium and lead, the oxides of manganese, the hypochlorites, and the sesquioxides of nickel and cobalt can be determined with excellent results. When barium or lead is present it is well to add a few cc. of hydrochloric acid.

WATER.—*The free oxygen and organic matter contained in natural waters compared.*—Th. Weyl and X. Zeitler.[2] The question to be answered was: Do the free oxygen and organic matter of such waters bear any fixed relation to each other? Seven waters were examined. The oxygen was determined by the method of Schützenberger, the organic matter by the method of Kubel. In five of the waters the oxygen was found to diminish as the organic matter increased. In the other two—the worst examined, this was not the case. It was therefore concluded that the quantity of free oxygen contained in waters, as already noted by others, is no measure of their excellence. It was found, moreover, that the quantity contained by one and the same water is not at all constant.

J. C. Thresh[3] describes a convenient form of apparatus for collecting the gases dissolved in water.

Determination of nitrates.—M. W. Williams[4] has found that the method of Gladstone and Tribe, if properly applied, yields excellent results. It was noticed that the time required for the reduction of a given quantity of nitrates varied in different waters, even when the conditions under which the reaction took place were apparently identical. This led to the suspicion that the rate of reduction is influenced by the character of the other constituents, and the suspicion was verified by the results of a systematic investigation upon standard solutions of nitrate of potassium. Carbonic acid, calcium carbonate and sulphate, sodium chloride and phosphoric acid were found to accelerate the reduction, while sodium hydroxide and carbonate and caustic lime retard it. The experiments were,

[1] Bulletin de la Soc. Chim. 35, 551.
[2] Zeitschrift für Physiolog. Chemie, 5, 10.
[3] Journal Chem. Soc. 1881, 399.
[4] Journal Chem. Soc. 1881, 100.

for the most part, performed at a temperature of 24°. At lower temperatures the reaction proceeds more slowly. In order to study the progress of the reduction, the ammonia and the nitrites were determined at stated intervals—the former by titration with Nessler's solution, the latter by the method of Griess. The relative quantities of these compounds found at the different stages of the reaction seem to justify the conclusion that the reduction consists of two distinct steps: 1. The conversion of the nitrates into nitrites. 2. The conversion of the latter into ammonia; and that but little ammonia is formed until after all of the nitrate has been reduced to nitrite. Hence the absence of nitrite indicates that the conversion of nitrate into ammonia is complete. The directions for the determination of nitrates in natural waters are as follows: "Some strips of zinc-foil or very thin sheet zinc are placed in a wide-mouthed stoppered bottle and covered with a 3 per cent. solution of copper sulphate. When the zinc has acquired a sufficient coating of copper, the solution is poured off and the copper-coated zinc washed free from zinc sulphate and drained. A portion of the water to be analyzed is then poured in and the couple rinsed with it in order to displace the adhering distilled water. The couple is again drained, and finally the bottle is filled with the water to be analyzed, the stopper inserted, and the whole allowed to digest in a warm place until the reduction of the nitrates is completed. The water may then be found turbid with floating particles of oxide of zinc; to remove these, it is poured off into a stoppered bottle and left at rest until the turbidity has subsided. A measured portion of the clear supernatant fluid is then withdrawn, diluted to the necessary extent, and the ammonia in it titrated by Nessler's method." About one square decimeter of zinc should be used for every 200 cc. of water containing 5 parts or less of NO_3 in 100,000. When the water is richer in nitrates a larger surface should be employed. The reduction may be hastened by raising the temperature to 30°, or even 40°; by the partial saturation of the water with carbonic acid; or by the addition of a small quantity of sodium chloride.

Perkins[1] estimates the nitrates in water by placing 100 cc. of it in a platinum dish, inserting a spiral of magnesium, adding a little fused chloride of sodium, and allowing the whole to stand until the magnesium has dissolved. The ammonia is then distilled off and determined by Nessler's solution.

Estimation of organic carbon and nitrogen simultaneously with the estimation of nitric acid.—In order to avoid the use of sulphurous acid in the Frankland process, which is in many ways objectionable, M. W. Williams[2] first reduces the nitrates by means of the zinc-copper couple in the manner already described. After complete reduction has been effected, the ammonia, and indirectly

[1] Analyst, 1881, 58, taken from Berichte der deutsch. chem. Gesellschaft, **14**, 1586.
[2] Journal Chem Soc. 1881, 144.

the nitric acid, is determined in a measured portion of the solution which is withdrawn for the purpose, or in the distillate obtained by concentrating the portion which is to serve for the determination of organic carbon and nitrogen. During the distillation, which is continued until the volume of the liquid has been reduced to 200 cc. or even less, one or two drops of a concentrated solution of sodium carbonate, or a small fragment of calcium oxide, is added to insure the complete removal of ammonia. If calcium carbonate is in the meantime deposited upon the sides of the retort, it is decomposed by means of phosphoric acid or a small quantity of sulphurous acid, which at this stage of the process can do no harm. The solution is then brought into a smooth hemispherical dish and evaporated to dryness. The combustion of the residue is effected in the manner prescribed by Frankland.

CHLORINE.—*Estimation of chlorine, cyanogen and sulphocyanogen in the same solution.*—W. Borchers.[1] From 10 to 20 grams of the mixed salts are dissolved in water and diluted to one litre. A portion of this solution is measured off, and the quantity of a standard silver solution required to exactly precipitate all three of the substances determined. To another equal portion is added the same amount of the silver solution. The precipitate, still moist, is treated with nitric acid having a specific gravity of from 1.37 to 1.40 and boiled. The undissolved residue contains all of the chlorine as silver chloride. A determination of the sulphuric acid in the filtrate gives the amount of the sulpho-cyanogen originally present. The cyanogen is then indirectly determined by estimating the silver in the filtrate by Volhard's method, and subtracting from the amount found a quantity equivalent to the sulphocyanogen. If ferrocyanogen is also present, it is first removed by adding a ferric salt free from chlorine, after which the filtrate is treated in the manner described.

PHOSPHORUS.—*Determination of phosphoric acid in phosphates.*—A. Grupe and B. Tollens[2] have undertaken an investigation of the conduct of phosphates towards citrate of ammonium, in order to ascertain (1) the cause of the solvent action of the latter, and whether there is an essential difference in its conduct towards different phosphates; (2) whether the determination of phosphoric acid in citrate of ammonium solutions by direct precipitation with magnesia mixture (method of Petermann) is sufficiently exact. They conclude that the solvent action is due to the formation of phosphate of ammonium and citrate of calcium which dissolves in the excess of citrate of ammonium. And the following facts are cited to justify the conclusion: (1) if a solution of phosphate in citrate of ammonium is allowed to stand or is evaporated, citrate of calcium crystallizes out; (2) crystals having the same appearance form at once when a solution of citrate of ammonium is poured on an

[1] Repert. der analyt. Chemie, 1881, 130, taken from Berichte der deutsch. chem. Gesellschaft, **14**, 1587.
[2] Berichte d. deutsch. chem. Gesellschaft, **13**, 1267.

excess of the phosphate; (3) citrate of calcium dissolves easily in citrate of ammonium, and alcohol precipitates from such solutions a double citrate of calcium and ammonium. They find moreover that tricalcium phosphate (Ca_32PO_4) is also soluble to a considerable extent in citrate of ammonium, though much less so than the dicalcium salt ($CaHPO_42H_2O$); and conclude, therefore, that there is no essential difference in the conduct of the citrate towards the so-called insoluble and reverted or precipitated phosphates. They suggest that the difference in the solubility of the two kinds of phosphates may be due to differences in their physical conditions.

In regard to the second question, namely, whether the method of Petermann gives sufficiently accurate results, they state that if three times the calculated amount of magnesia mixture is added to the solution of phosphate in citrate of ammonia, the precipitation of the phosphoric acid is nearly complete; but the precipitate contains calcium, rendering its solution in hydrochloric acid and reprecipitation by ammonia necessary. If a still larger proportion of the magnesia mixture is added, the precipitation of the phosphoric acid is incomplete; but the precipitate contains calcium and an excess of magnesium. These errors may or may not compensate each other.

A. Herzfeld and G. Feuerlein,[1] on the other hand, believe that the solvent action of the citrate is due to the formation of phosphate of calcium ammonium (NH_4CaPO_4) which dissolves in the excess of citrate of ammonium. They observed, like Grupe and Tollens, that the precipitate obtained from citrate solutions of phosphate by magnesia mixture always contains calcium. At first they ascribed its presence to the absorption of carbonic anhydride from the air by the ammoniacal solution, but concluded that this could not be the case, having found that carbonic anhydride does not precipitate calcium from solutions of calcium citrate or phosphate in ammonium citrate. Neither is the calcium which is found in the precipitate, there in the form of citrate; for the authors were unable to detect the presence of orthophosphates in the ignited precipitate by means of the silver reaction. The precipitate after ignition contains only pyrophosphates, which could not be the case if it had previously contained either carbonate or citrate of calcium. The conclusion is, therefore, that the calcium is precipitated as phosphate of ammonium calcium (NH_4CaPO_4) when the strongly ammoniacal magnesia mixture is added; and the following facts are given as confirming this view: (1) If ammonia gas is conducted into a concentrated solution of ordinary phosphate of sodium, phosphate of ammonia sodium ($NH_4Na_2PO_4.12H_2O$) is precipitated; (2) if a sufficiently concentrated solution of dicalcium phosphate ($HCaPO_4.2H_2O$) in citrate of ammonium is treated in the same manner or with a concentrated solution of ammonia, phosphate of ammonium calcium ($NH_4CaPO_4.xH_2O$) is precipitated. The citrate of ammonium solution employed by the authors was not that recom-

[1] Zeitsch. für analyt. Chemie, 1881, 191.

mended by Petermann. It was neutral instead of alkaline, and had a specific gravity of 1.105 instead of 1.09.

Grupe and Tollens[1] reply that in the absence of any direct statement upon the subject it is impossible for them to know how Herzfeld and Feuerlein have applied the silver test to detect the presence of orthophosphates in the ignited precipitate, but their own experiments, made upon solutions of ortho- and pyrophosphates of sodium, show that the yellow color indicative of the presence of the former does not distinctly appear when the proportion of orthophosphate is less than 10 per cent. If the solution is warmed the test is more sensitive, especially at the moment when the alkaline reaction of the solution disappears. But the reaction is uncertain even in warmed solutions, and it could sometimes be obtained in solutions of pure pyrophosphate. Any reaction for orthophosphoric acid obtained by dissolving the ignited precipitate in nitric acid, neutralizing with ammonia and adding nitrate of silver, would be indecisive, because of the known tendency of pyrophosphoric acid in the presence of nitric to pass into orthophosphoric acid. The silver nitrate test is, however, very sensitive when the solid material is simply moistened with the nitrate. If the ignited precipitate in question is tested in this manner it becomes decidedly yellow, showing the presence of orthophosphate. The objections of Herzfeld and Feuerlein to the views of the authors are therefore not valid, so far as they are based on the supposed absence of orthophosphates from the precipitate after ignition. Finally, the fact that a precipitate consisting of ammonium calcium phosphate was obtained from the citrate solution in the manner described by Herzfeld and Feuerlein is no proof that such a compound existed in the solution previous to precipitation.

A. Koenig[2] calls attention to a very serious defect of citrate of ammonium as a solvent for reverted phosphates—namely, the fact that widely varying percentages of phosphoric acid are obtained when different weights of any given material are treated with the same amount of citrate. One gram of material treated according to Petermann's method yielded 30.08 per cent. of phosphoric acid, while two grams of the same material treated in the same manner with an equal amount of the citrate solution yielded only 25.12 per cent. In another case one-half gram gave 19.20 per cent. of phosphoric acid, while a whole gram gave only 12.80 per cent. The method of Fresenius, Neubauer and Luck gave similar and nearly equal differences. In order to obtain even relatively correct results it is necessary that the quantity of citrate used should always have a fixed proportion to the amount of reverted or precipitated phosphates to be dissolved, which is practically impossible. The point is an important one in view of the fact that there is lack of uniformity in the recommendations of different authorities as to the

[1] Berichte d. deutsch. chem. Gesellschaft, **14**, 1042.
[2] Zeitsch. für analyt. Chemie, 1881, 40.

quantity of material to be employed for the determination of phosphoric acid.

R. Hercher and P. Wagner[1] confirm the statement of Koenig, and observe, further, that the citrate is relatively less efficient as a solvent for so-called superphosphates than for precipitated phosphates, because of the presence in the former of large quantities of calcium sulphate, which must also be decomposed and dissolved at the expense of the citrate. They find, however, that this difficulty can be obviated by using ammonium oxalate in connection with the citrate. They conclude with reference to Petermann's method of direct precipitation from the citrate solution, that a portion of the phosphoric acid remains in solution, but if previous to solution it was in combination with non-volatile elements such as sodium, iron or calcium, especially the last, enough of these are precipitated to partially or even over-compensate for the unprecipitated phosphoric acid.

In view of the established objections to the use of citrate of ammonium in phosphate analyses: (1) that it dissolves tricalcium phosphate to a considerable extent; (2) that phosphoric acid cannot be completely precipitated from it by means of magnesia mixture; (3) that the precipitate nevertheless contains calcium and an excess of magnesium, though there is no certainty that their presence will compensate for the unprecipitated phosphoric acid; (4) that, in the presence of magnesium, the phosphate of ammonium-magnesium is apt to escape solution; (5) that varying percentages of phosphoric acid are dissolved when different weights of the same material are treated with a fixed amount of it; (6) that its action varies according as it is acid, neutral or alkaline,—Grupe and Tollens[2] recommend that a dilute (0.25 per cent.) solution of citric acid be employed in its stead. Like the citrate, it dissolves the tricalcium phosphate to a greater or less extent, according to its physical condition, but the authors apparently do not hope to find a reagent free from this objection. It dissolves the dicalcium and ammonium-magnesium phosphates with great ease, and vigorously attacks the phosphate of iron and aluminium. Its action is quite uniform, that is, a given amount of it will dissolve from two grams of material nearly the same percentage of phosphoric acid as from one. The phosphoric acid can be precipitated from it directly by molybdate, though this method is sometimes attended with a loss of 0.2–0.3 per cent. In order to obtain exact determinations of the phosphoric acid the authors recommend that the solution, whether citrate of ammonium or citric acid has been employed as the solvent, be evaporated with an excess of calcium oxide and the organic matter finally destroyed by heating the residue in a muffel. In this way a white ash is obtained without loss of material, and all the difficulties mentioned by Fresenius, Neubauer and Luck as attending the combustion with carbonate of sodium, saltpeter, etc., are avoided. H. N. MORSE.

[1] Versuchs-Stationen, **27**, 1,

[2] Berichte der deutsch. chem. Gesellschaft, **14**, 754.

RESEARCHES ON THE RELATION BETWEEN THE MOLECULAR STRUCTURE OF CARBON COMPOUNDS AND THEIR ABSORPTION SPECTRA.[1]

In 1872 W. H. Hartley was led to these investigations by a desire to repeat and to carry out in a more complete manner the experiments of Miller, whose method of investigation and the results attained were published in 1863.[2] The end sought in this repetition of Miller's experiments was to find out what relation, if any, exists between the molecular constitution and the actinic absorption of organic substances. In his statement of results Miller says, "I have not been able to trace any special connection between the chemical complexity of a substance and its diactinic power"; so that very little inducement was offered to a continuance of these investigations. The difficulty of obtaining substances sufficiently pure for experiments of this nature is very great, and Dr. Hartley states that notwithstanding the extreme care taken in their purification, some of the substances examined by Miller were impure.

In 1872 (at which time Dr. Hartley and Prof. A. K. Huntington were associated in this work) Dr. Miller's apparatus was reconstructed and certain improvements were introduced. After some time spent in trying the various methods of studying the ultra-violet rays, the photographic method was selected as being decidedly the most satisfactory.

The instruments used were the following:

1st. An induction coil and Leyden jar for producing an unbroken stream of sparks between metal points. 2d. A collimator tube 3 feet long, carrying a pair of clips at one end for holding the points close to the slit, and a quartz lens at the other. 3d. A quartz prism placed at the angle of minimum deviation for the sodium line *D*. 4th. Another quartz lens, and the body of a photographic camera which could be extended to 36 inches. The fact that the lines of cadmium in the ultra-violet, as well as in the visible portion of the spectrum, have been measured and their wave-lengths calculated (by M. Mascart) has caused Hartley to adopt them as lines of reference in defining the position of absorption bands.

A complete description of the method of investigation and an account of some of the results reached by Hartley and Huntington were published in 1879.[3]

These results are summarized as follows:

1st. Every increment of CH_2 in a homologous series of alcohols and of acids effects an absorption of the more refrangible of the ultra-violet rays, so that the greater the number of carbon atoms in the molecule the shorter is the transmitted spectrum. 2d. Ter-

[1] Abstract of a paper in Journal Chem. Society, 1881, 153.
[2] Miller, On the Photographic Transparency of Various Bodies, etc., Phil. Trans. 1863, I.
[3] Phil. Trans. Part I, 1879.

penes with the composition $C_{10}H_{16}$ possess in a high degree the power of absorbing the ultra-violet rays of the spectrum, though they are inferior in this respect to benzene and its derivatives. Terpenes with the composition $C_{15}H_{24}$ have a greatly increased absorptive power, as shown by the greater extent to which they suffer dilution before the transmission of all rays is attained. 3d. Benzene and its derivatives, in addition to abnormally great absorptive power, show the peculiarity of *absorption bands* when dilute solutions are examined.

These results were attained by the examination of a very large number of substances of varied character. A consideration of the facts developed forced the investigators to the conclusion that *banded spectra* are caused by the compact molecular structure attributed by chemists to the double linking of three pairs of carbon atoms in a closed chain.

At this stage of the work the effect of various atomic groupings upon ultra-violet absorption was investigated. Ethylene, amylene, and allyl alcohol were examined, to ascertain whether bodies supposed to contain two adjacent carbon atoms doubly linked show any peculiarities in their absorption spectra. In the case of ethylene very little absorption was noticed. Carefully rectified amylene undiluted showed an absorption extending as far as the line *Cd* 17 wave-length = 274.34 (Mascart).

On diluting the liquid with pure alcohol to degrees varying between $\frac{1}{10}$th and $\frac{1}{1000}$th of the original volume, no intermediate absorption appeared. In the case of allyl alcohol no absorption bands were seen. A large number of isomeric alcohols, secondary and tertiary, were examined, but no absorption bands were noticed in any case.

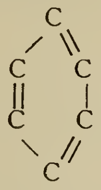
To investigate the effect of the supposed treble linking of adjacent carbon atoms, acetylene was selected, being a substance easily prepared, and supposed moreover to be nearly related to benzene, on account of the ease with which it may be converted into the latter. An absorption extending to the line *Cd* 23 was revealed, but no absorption bands appeared. The experimenter's deduction from the examination of a large number of substances is, that "in all cases where the carbon atoms are supposed to be arranged in an open chain, no absorption bands are seen."

The occurrence of the absorption bands is in all cases independent of the arrangement of the hydrogen and oxygen atoms. No bands are caused by the replacement of hydrogen by various groups, such as NH_2, OH, etc., or by the halogens, when the result is a colorless body.

The next portion of the investigation is "*On the nature of actinic absorption exerted by various closed chains of carbon atoms.*"

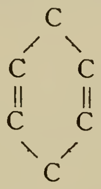
With hydrocarbons containing at least six atoms of carbon, four arrangements of a symmetrical character are possible which admit of the carbon atoms forming a closed chain.

1st. Three pairs of carbon atoms may be doubly linked, as in Kekulé's formula for aromatic compounds generally.



2d. Each carbon atom may be directly combined with three other carbons, as in Ladenburg's prism formula.

3d. Two pairs of carbon atoms may be doubly linked, as is generally assumed to be the case in turpentine oil.



4th. The six carbon atoms may be singly united with each other, as in benzene hexachloride.

All substances which may be represented by either of the first two formulae show absorption bands in the spectra transmitted by dilute solutions. When the hydrogen atoms in benzene are replaced by alcohol radicals, or by the groups OH, NH_2, COOH or NO_2, bands still appear, but are modified first by a fusion of several narrow bands into one broad band, and second by an increase in the intensity of the absorption. The general conclusion here deduced is as follows:

"*The presence of absorption bands in the ultra-violet spectra transmitted by compounds of the aromatic series, is due to the particular arrangement of the six carbon atoms, forming the nucleus of the molecules of such compounds.*"

As an example of the third formula above given, turpentine oil was selected, and its examination revealed no absorption bands; the examination of about fifty essential oils showed that the terpenes when pure exert no selective absorption on the rays of the ultra violet spectrum.

Hence, assuming that terpenes have a nucleus in accordance with the third arrangement, it follows that: "*A closed chain of carbon atoms in which only two pairs of contiguous atoms are doubly linked, does not give rise to absorption bands.*"

As examples of compounds containing a closed chain of six atoms *singly linked*, camphor and camphoric acid were chosen. Various formulae for these substances have been proposed, namely

by Kekulé, Hlasiwetz, Kachler and Wreden. Kekulé's formula represents in each of these compounds a pair of adjacent carbon atoms *doubly linked;* the other three, however, agree in the point that there is a group or nucleus of six carbon atoms *singly linked;* all four agree in representing the nucleus as a closed chain. Solutions in alcohol of camphor and camphoric acid were prepared, varying between the limits $\frac{1}{10}$th and $\frac{1}{150}$th in the case of camphoric acid, and in the case of camphor to the minimum limit $\frac{1}{1000}$th. None of these solutions showed any absorption bands.

Benzene hexachloride is a typical example of a body containing six carbon atoms singly linked, and the examination of this substance was regarded as the crucial test of the correctness of previous deductions, the expectation in the case of this substance being, as also with camphor and camphoric acid, great freedom from absorption bands. The result of the examination of this substance proved the remarkable transparency of the substance and the entire absence of absorption bands.

Julius Thomsen has recently shown that the heat of combustion of benzene, if the carbons are linked as in Kekulé's formula, would amount to 846,040 heat units, whereas if there are nine single linkings in the molecule it would be 802,330 units. The experimental number obtained by Thomsen is 805,800; hence he concludes that the six carbon atoms in benzene are nine times singly linked with each other. Subject to the correctness of this deduction, the following conclusion is considered to be established:

"*No molecular arrangement of carbon atoms causes selective absorption unless each carbon is itself united to other three carbon atoms as in the case of benzene.*"

The investigation of naphthalene, anthracene and phenanthrene was then undertaken, with the expectation that the spectra of these substances would show a larger number of bands of greater intensity than appear in the spectrum of benzene. The constitution of naphthalene is generally represented by the fusion of two benzene nuclei, and that of anthracene and of phenanthrene by the fusion of three such nuclei. The anticipation was therefore natural, and was moreover to some extent satisfied by actual experiment. Dilutions in alcohol of naphthalene varying between $\frac{1}{1000}$th and $\frac{1}{100000}$th of its weight, and in the case of anthracene and phenanthrene to the limits $\frac{1}{2000000}$th and $\frac{1}{50000000}$th of their weight of substance, were examined, and their spectra photographed.

In the hydrocarbons, benzene and the three just considered, the most prominent feature common to all the spectra is the group of four strong absorption bands, situated in the case of benzene in the most refrangible part of the spectrum, lowered in refrangibility in the case of naphthalene, and still further reduced in the cases of anthracene and phenanthrene.

In similar order the intensity of the absorption is increased, being at least forty times greater in the case of naphthalene than in benzene.

The next portion of the paper is: "*On the cause of absorption bands in the spectra transmitted by benzene and its derivatives.*"

In the absorption of the ultra-violet rays by hydrocarbons of the aromatic series we have two kinds of absorption manifested, namely a *general* absorption and a selective absorption. It is the selective absorption which distinguishes these from all other classes of carbon compounds. The absorptive power of alcohols and of fatty acids is dependent upon the number of carbon atoms in the molecule, while in aromatic compounds it depends entirely upon the *structure of the molecule.*

When a molecule of a substance is capable of vibrating synchronously with a radiation, the ray received on the substance is absorbed. The absorption is complete if the *direction* of vibration of the ray and of the molecule is the same, but the *phase* opposite. It is evident that general actinic absorption, exerted by carbon compounds, is due to the vibration of the molecules, since absorption increases in extent with the number of carbon atoms in the molecule; or, in other words, the larger the molecule the lower its rate of vibration. Selective absorption appears to be caused by the vibration of atoms within the molecule.

When a substance like benzene absorbs all rays beyond a certain refrangibility, it is because the molecules are vibrating synchronously with certain rays, and the number of molecules present is sufficient to damp all vibrations. When the liquid is diluted the number of molecules present is not sufficient to damp all the vibrations and some rays are transmitted. If, however, certain carbon atoms within the molecule are vibrating synchronously with certain rays, we shall have selective absorption of these rays after the general absorption has been so weakened by dilution as to allow them to pass.

The mean rate of vibration of the rays absorbed by naphthalene and anthracene is less than that of the rays absorbed by benzene. It follows from this that the bands in benzene, naphthalene and anthracene, though conceived to be caused by the vibration of the carbon atoms within the molecule, are not independent of, but are a consequence of the molecular vibrations; they must, in fact, be regarded as harmonics of the fundamental or molecular vibrations.

Musical instruments of the same construction, set in vibration in the same way, will always evolve tones of the same quality or wave form. Hence in the examination of molecular vibrations, as the same method of actuating the vibrations is always employed, the difference in wave-form must indicate a difference in structure, that is to say, in chemical constitution.

"It is easy to predict from this that as the wave-form must manifest itself in a variety of absorption bands, not only may substances be classified according to their transmitted spectra, but we may ascertain their chemical constitution; and if the bodies in question be isomerides, doubtless further research will enable us at once to determine whether they be ortho-, meta- or para-derivatives."

W. C. D.

NOTES.

A New Gas-Regulator.

The essential principles of this device are but little different from those of a great many others that have appeared within the last few years, and the writer claims for it no great amount of originality, except perhaps for the mechanical details of its construction, which he has endeavored to simplify as far as possible.

The construction of the regulator will be best understood by reference to the diagram. It consists essentially of three parts: a

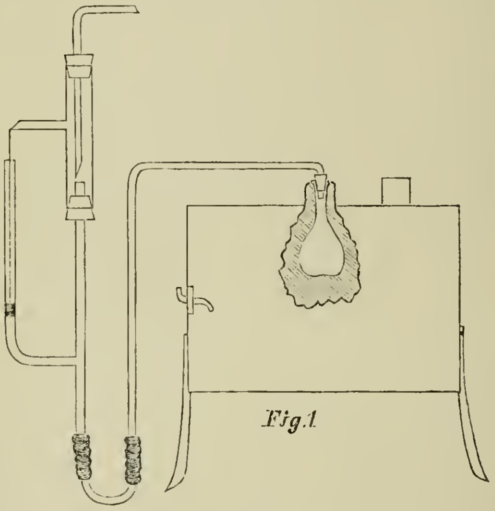


Fig.1

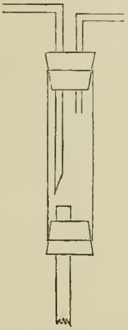


Fig.2

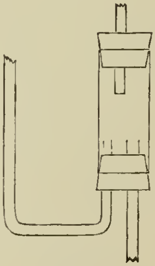


Fig.3

small glass flask used as an air chamber; a U tube, one limb of which is of rather small bore, while to the other, which is of larger tubing, is attached the apparatus for regulating the temperature; the tube through which the gas passes.

The air chamber may consist of flasks of different capacities, the larger ones for work at low temperatures, and the smaller ones for high temperatures. The lower end of the U tube is best made so that it may be attached to its limbs by means of pieces of rubber tubing, thus enabling us to lengthen the U tube when it is desired to increase the range of available temperature. The tube for the passage of the gas is similar to that in Bunsen's regulator, except that the inlet tube has its lower end beveled and is held in place by a rubber stopper. The desired temperature is attained by the use of the plunger in the small tube to the left. The plunger is made from a piece of very small glass tubing, a sole-leather disc of the proper size, a pin and some sealing-wax. If covered with some lubricating substance, such as water, glycerin, etc., it will be found to work much more easily.

The entire apparatus may be made without any glass-blowing beyond the mere bending of tubes, by the aid of the devices suggested in figs. 2 and 3.

To use the regulator, fill it with mercury until both limbs of the U tube are nearly full; if used with an air-bath, place the flask in the bath, as in the diagram, and by the use of the plunger produce the temperature desired, after which the instrument will automatically maintain this temperature for any length of time.

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Concerning the Halogens.

In the course of the investigations of Victor Meyer on the specific gravity of chlorine at high temperatures, it was observed that in a number of experiments a small quantity of oxygen was obtained from the chlorine after it had been heated. These observations led to a careful examination of the subject, particularly with reference to the possibility of getting oxygen from chlorine. H. ZÜBLIN has just communicated the results of his studies. He found that, whenever a particular kind of porcelain—that from Bayeux—was used, oxygen was obtained; whereas, when vessels of platinum or of Berlin porcelain were used, no oxygen was obtained. By means of complicated and elaborate experiments it is proved that the oxygen obtained is a result of the action of the chlorine at high temperatures on the Bayeux porcelain. Attempts were made to separate the possible constituents of chlorine by diffusion. The diaphragms used were made of platinum, in which very fine holes were bored by means of a steel needle. No separation of chlorine into simpler bodies could be effected even at the

highest temperatures. Similar results were obtained with iodine and bromine. The paper concludes with this remark: "As the result of the work described, it may be stated that in spite of the most varied and the most favorable conditions for the separation of oxygen from the halogens, no observations were made which can in the least support the view that oxygen is contained in the halogens."—(*Annalen der Chemie*, **209**, 277.)

On the Synthetical Production of Urea from Benzene, Ammonia and Air by the Action of Heated Platinum.

E. F. Herroun describes some experiments undertaken by him as follows: "Air was drawn by means of an aspirator through washing bottles containing (1) ammonia and (2) benzene, the glass tubes conveying the air dipping below the surface of the liquid in both bottles, then through a tube containing a helix of platinum wire, heated to dull redness by a Bunsen burner, and finally through water contained in potash bulbs to absorb the products of the action.

"On analysis, the water at the end of the experiment was found to contain ammonium carbonate, nitrite, and nitrate; but it was also observed that a solid crystalline substance had collected in the tube containing the platinum, depositing not far from the heated wire. On analyzing this substance qualitatively it appeared to be ammonium cyanate, giving the following reactions: When treated with dilute sulphuric or hydrochloric acid it evolved cyanic acid, recognized by its odor. Its solution gave with silver nitrate a white precipitate, soluble in dilute nitric acid, and converted by hydrochloric acid into silver chloride, with evolution of cyanic acid. After boiling its aqueous solution and evaporating to a small bulk, it gave with strong nitric acid a crystalline precipitate, soluble in potash solution, and evolving ammonia when boiled with it, indicating its conversion into urea." Analysis showed that the substance finally obtained had the composition of urea.—(*Journal Chem. Soc.* 1881, 471.)

On Sewage in Oysters.

C. A. Cameron has lately examined oysters taken from the "beds" on the northern shore of the bay of Dublin, the water of which is yearly becoming more polluted with excrementitious and other offensive matters. The oysters were taken from a place where the tide covers them to a height of about ten feet, and which during low water is nearly dry. In most of the oysters the brine had no peculiar odor; but in a rather large proportion there was a very slight but distinctly foetid odor, whilst in a few cases there was a strong and unmistakable odor of sewage. Examined micro-

scopically, the liquid in the oysters which had a foetid odor was found to swarm with micrococci and other low organisms similar to those usually present in sewage. The water of the bay was examined at low tide, and it was found to be highly charged with sewage matter. Any one may satisfy himself that sewage is constantly discharging over fore-shores, in which various edible molluscs have their abiding-place; and it is in the highest degree improbable that animals can always resist successfully the entry of polluted brackish water into their calcareous dwellings. It may be that the illness which so many persons have experienced after eating oysters, believed to have been stale, was really due to the presence of sewage matter in the juice of the molluscs.—(*Chem. News*, **44**, 52.)

The Action of Compounds inimical to Bacterial Life.

W. M. HAMLET has examined the behavior of bacteria when exposed to a variety of substances, including such as are classed as disinfectants and those which are poisonous to higher animals. The examination consisted in providing bacteria with the conditions necessary for growth, and noting the interruption to their normal development upon the addition of one or another substance. Beef tea, extract of meat, Pasteur's fluid, hay infusion, and other solutions capable of furnishing the required nourishment, were boiled to render them free from previously existing forms of life, and then impregnated with definite species of bacteria, usually *Bacteria termo* or *Monas crepusculum*. Small flasks were about half filled with these solutions and kept at a temperature of 25°C. The action of various gases was first determined.

Pure hydrogen was passed over the liquid in a flask. On examination at the end of three days the solution contained bacteria in abundance. Oxygen, carbon monoxide, marsh gas, nitrogen and sulphuretted hydrogen were likewise incapable of checking bacterial growth. Chlorine, nitric oxide and sulphur dioxide, on the other hand, left no trace of living bacteria in solutions through which they were passed. The addition of hydrogen peroxide was also fatal.

Various salts and organic acids were next experimented with, and the following compounds among others were found to have no decided effect when used in the form of five per cent. solutions, the bacteria developing readily in all of them: Potassium carbonate, ammonia, olive oil, castor oil, cod-liver oil, acid potassium sulphite, ammonium sulphate, acid potassium tartrate, benzoic acid, citric acid, oxalic acid, potassium iodide, potassium bromide, potassium permanganate, potassium chlorate, sodium hyposulphite, succinic acid, laudanum, potassium formate, tannin, acetic acid.

The following compounds were found to have effect upon bacteria, hindering their growth but not preventing their ultimate

development: Potassium and ammonia alums, ferrous sulphate, ferric chloride, magnesium and aluminium chlorides, bleaching powder, camphor, salicylic acid, chloroform, creosote and carbolic acid.

In these cases the bacteria became very sluggish in their movements. Another and more elaborate series of experiments with chloroform, creosote and carbolic acid only confirms the above result, and goes to show that bacteria may be kept in an inactive state for some time by the aid of the second class of compounds, but that they will proceed with their regular development when removed to favorable surroundings.

The author states that the best disinfecting agents are, in general, those capable of exerting an immediate and powerful oxidizing action, and that it is active oxygen, whether from the action of chlorine, nitric oxide or hydrogen peroxide, which must be regarded as the greatest known enemy to bacterial life.—(*Journal Chem. Soc.* 1881, 326.) D. T. D.

On a Suitable Reagent for distinguishing Ptomaïnes from Vegetable Alkaloids.

Ptomaïnes, or alkaloids found in the human cadaver, present in general the most important chemical characteristics and physiological properties of the vegetable alkaloids, and may for that reason readily be mistaken for them. Such a mistake in fact occurred recently in Italy, the experts deciding that a certain individual had been poisoned by delphinine, when in reality the substance pronounced by them to be delphinine was found to be simply a ptomaïne resembling it. The rational way to distinguish in such a case between a ptomaïne and a vegetable alkaloid is evidently to determine all of the chemical and physiological properties of the suspected poison which has been isolated. If it is found to lack one or more of the known characteristics of the vegetable alkaloid, the presence of which seems to be indicated by other experiments, then the compound under examination is not that alkaloid, but probably a ptomaïne resembling it. This method, although the most sure, is inconvenient, and moreover can only be employed when the quantity of the suspected substance isolated is sufficient to allow of a complete study.

P. Brouardel and E. Boutury have devised a means of deciding the point, which is at the same time easy of application and reliable. Ferricyanide of potassium, when treated with a solution of a pure vegetable alkaloid, is unacted upon by it; while under the same conditions it is instantly reduced to the state of ferrocyanide by a ptomaïne and thus becomes capable of forming Prussian blue with a ferric salt. The method of applying the test is as follows: The base extracted from the cadaver, by the method

of Stas is converted into the sulphate, and a few drops of its solution placed in a watch-glass containing a few drops of solution of potassium ferricyanide. A drop of neutral ferric chloride added to this mixture produces a precipitate of Prussian blue, if the base isolated is a ptomaïne, while no such effect is produced if it be a vegetable alkaloid. Up to the present but two exceptions to this general rule have been found—morphine, which readily reduces potassium ferricyanide, and veratrine, which gives traces of such reduction. It is possible, however, that in this last case the reducing action is due to certain impurities which the investigators were unable to completely remove from the veratrine employed by them.—(*Comptes rendus*, **92**, 1056.) R. D. C.

On the Transformation of Morphine into Codeïne and Homologous Bases.

The formula of morphine, $C_{17}H_{19}NO_3$, and that of codeïne, $C_{18}H_{21}NO_3$, show that these two bases differ from each other by CH_2, and that codeïne may be considered as derived from morphine by the substitution of a CH_3 group for one atom of hydrogen. An English chemist, How, tried in 1853 the action of methyl iodide upon morphine, but he obtained an isomere of the hydriodate of codeïne, presenting none of the characteristics of an alkaloid salt. More recently Matthiessen and Wright have determined something of the relation of morphine to codeïne. By heating morphine with hydrochloric acid they extracted the elements of water, and obtained as a result apomorphine. Codeïne submitted to the same treatment likewise yielded apomorphine and also methyl chloride. There is therefore present in morphine an alcoholic OH group, and in codeïne a group OCH_3. In considering the various reactions of morphine it was observed by E. Grimaux that it resembled the phenols in its characteristics, and it occurred to him that codeïne might be the methyl ether of morphine considered as a phenol. It then only remained to try this transformation by the usual means, viz. heating with alcoholic potash or soda. Morphine was dissolved in alcoholic soda solution, the proportions being one molecule of morphine to one molecule of soda, and a quantity of methyl iodide corresponding to two molecules added. On gently heating the mixture brisk action took place, which ceased after a few minutes. The reaction took place in the manner expected, but was complicated by a secondary reaction, and in place of free codeïne there was obtained the iodomethylate of codeïne, $CH_3I.C_{17}H_{18}NO_2(OCH_3)$. At the same time that double decomposition took place between one molecule of the methyl iodide and the morphine, a second portion of the methyl iodide united directly with the molecule. The compound thus obtained was identical in every respect with the addition product of codeïne and methyl iodide.

On repeating the experiment, reducing the proportion of methyl iodide to half of that employed in the first operation, free codeïne was obtained; but the yield was very small,—20 grams of morphine yielding but 2 grams of hydrochlorate of codeïne. The codeïne thus obtained possessed the same crystalline form and all of the chemical characteristics of that extracted from opium, and was found to be in every respect absolutely identical with it. Upon operating with ethyl, in the place of methyl iodide, there was obtained a new base, $C_{19}H_{23}NO_3$, homologous with codeïne, which is the ethyl ether of morphine, considered as a phenol. This new base can be obtained in fine crystals, fusing at 83°, readily soluble in ether and alcohol, and a little less soluble than codeïne in boiling water. Its yield is from 40 to 45 per cent. of the weight of the morphine employed.

From morphine there can then be obtained a series of compounds of which codeïne is the type, a series numerically as great as the series of ethers from an alcohol. To this class of compounds M. Grimaux proposes to give the generic name of *codeïnes*, the codeïnes being the ethers of morphine. The methyl ether is *codomethyline*, or more simply codeïne, its homologue just described *codoethyline*, and so on. M. Grimaux announces his intention of preparing other compounds of this series, which appears to him to furnish an interesting subject of study to physiologists. —(*Comptes rendus*, **92**, 1140.) R. D. C.

Alleged Ozone as a Preservative.

"Ozone" has been largely advertised within a few months as a new preservative for all kinds of animal and vegetable substances. The gas is produced by the combustion of a fine dark powder of cinnamon odor. This substance consists of sulphur mixed with a little carbonaceous matter. On burning, only 0.09 per cent. of ash remained.

These results are offered without waiting to complete the examination, because the so-called ozone is clearly shown to be sulphurous anhydride, whose destructive action on the germs of fermentation has long been well known.

R. B. WARDER.

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ON THE PROPYL DERIVATIVES AND DECOMPOSITION PRODUCTS OF ETHYL ACETOACETATE.[1]

BY BEVERLY S. BURTON.

Preparation of Monopropylethyl Acetoacetate.

This was prepared according to the modified process of Conrad and Limpach.[2] 27 grams of sodium were dissolved in 270 grams of absolute alcohol, then 152.7 grams of ethylacetoacetate were added, and gradually 206 grams of propyliodide. This mixture was then heated for several hours on the water-bath with an inverted condenser until it was perfectly neutral. The alcohol was then distilled off, and a sufficient quantity of water added to dissolve the separated sodium iodide. The oily liquid product thus formed was then, in a separating funnel, separated from the aqueous solution, the former was washed with water, dried with calcium chloride and subjected to repeated fractional distillation. In this manner 117 grams of a clear, limpid liquid, boiling between 205° and 210°, of a pleasant ethereal odor, were obtained. By far the greatest portion distilled between 208° and 209°. Its specific gravity was 0.981 at 0°, compared with water at 4°. The combustion gave the following results:

[1] From the author's Dissertation, Würzburg, 1881.

[2] Ann. Chem. Pharm. 192, 153.

I. 0.2554 gram substance yielded 0.5839 gram CO_2 and 0.2192 gram H_2O.

II. 0.1761 gram substance yielded 0.4052 gram CO_2 and 0.1526 gram H_2O.

	Calculated.	Found. I.	Found. II.
C_9	62.79	62.35	62.75
H_{16}	9.30	9.57	9.63
O_3	27.91	...	...
	100.00		

Corresponding to the formula of monopropylethyl-acetoacetate $\left\{\begin{array}{l} CH_3 \\ CO \\ CH(C_3H_7) \\ CO.OC_2H_5. \end{array}\right.$

Preparation of Dipropylethyl Acetoacetate.

The method of preparation in this instance was in every respect similar in principle to that employed and above described, with the exception that here the monopropylethyl acetoacetate was used instead of ethylacetoacetate. 27 grams of sodium were dissolved in 270 grams of absolute alcohol as before; 202.2 grams monopropylethyl acetoacetate added, then 200 grams of propyliodide. Out of the separated oily liquid, 119 grams, boiling between 235° and 236°, were obtained by fractional distillation.

The analyses yielded the following results:

I. 0.1978 gram substance 0.1876 gram H_2O; 0.4866 gram CO_2.

II. 0.1377 gram substance 0.1292 gram H_2O; 0.3377 gram CO_2.

	Calculated.	Found. I.	Found. II.
C_{12}	67.29	67.09	66.88
H_{22}	10.28	10.54	10.42
O_3	22.43	...	...
	100.00		

From which is calculated the formula $\left\{\begin{array}{l} CH_3 \\ CO \\ C(C_3H_7)_2 \\ CO.OC_2H_5 \end{array}\right.$. The dipropylethyl acetoacetate is very similar to the monopropyl substitution product. It is a coloress, limpid liquid, of pleasant odor, boiling

point 235–236°. Specific gravity 0.9585 at 0°, compared with water at 4°.

Saponification of Mono- and Dipropylethyl Acetoacetate.

It was first shown by Geuther[1] in 1865 that ethylacetoacetate when subjected to the action of alkalies, undergoes decomposition, and yields acetone, carbon dioxide and alcohol. Later the researches of Frankland and Duppa[2] proved that this decomposition held true not only for ethylacetoacetate, but for all alkyl derivatives of the same, expressed by the following equation:

$$\begin{matrix} CH_3 \\ CO \\ C(XY) \\ CO.OC_2H_5 \end{matrix} + 2KOH = \begin{matrix} CH_3 \\ CO \\ C(XY)H \end{matrix} + K_2CO_3 + C_2H_5.OH.$$

Wislicenus[3] now showed that at the same time with this above mentioned, there occurs a second decomposition, by which acetic acid is always formed, or in case an alkyl substitution product is subjected to the reaction, an alkyl substituted acetic acid is also formed in accordance with the following equation:

$$\begin{matrix} CH_3 \\ CO \\ C(XY) \\ COOC_2H_5 \end{matrix} + 2KOH = \begin{matrix} CH_3 \\ COOK \end{matrix} + \begin{matrix} C(XY)H \\ COOK \end{matrix} + C_2H_5.OH.$$

He found that the relative amounts of ketone and organic acid that are formed are dependent not only upon the substituted radical, but also upon the concentration of the alkali employed. In the method for the quantitative saponification[4] is established, that the amount of ether which is split up into two molecules of organic acids is greater the more concentrated the employed alkali, and the more concentrated the alkali remains after the saponification is effected. On the contrary, the more carbondioxide and ketone are formed the more dilute the employed alkali is.

The following experiments were made according to the above mentioned method of Wislicenus. Monopropylethyl acetoacetate boiling between 208°–209°, and dipropylethyl acetoacetate boiling at 235.5°, were employed.

[1] Jahresbricht, 1865, 302.
[2] Ann. Chem. **135**, 217.
[3] Ann. Chem. **186**, 161.
[4] Ann. Chem. **190**, 257–281.

Observations.

	10 cc. KOH sol. = cc. HCl. 10 cc. HCl = 0.0351 gr. HCl.	Emplo'd Ether.	Potash.	Diluted to 100 cc. 10 cc. yielded CO_2	t°	Bar	require HCl	CO_3	TOTAL. Ether decomp. in Organic Salts.	Ketone and CO_2	KOH in Organic Salts.
	cc.	gr.	cc.	cc.		mm	cc.	gr.	gr.	gr.	gr.
Propylethyl acetoacctate with 10 per cent. KOH sol.	18.70	1.72	17	17.26	11.8	747	2.64	0.3198	0.4434	1.2502	0.2892
" 20 " " " I	36.50	1.72	9	13.05	10.	745	2.36	0.2427	0.7639	0.9487	0.4983
" 20 " " " II	36.50	1.72	9	11.76	9.4	745	2.29	0.2192	0.8236	0.8567	0.5372
Dipropylethyl acetoacetate with 10 per cent. KOH sol. I	18.38	2.14	17	8.30	15.	741	1.91	0.1509	1.2516	0.7337	0.6562
" 10 " " " II	18.38	2.14	17	8.77	15.	741	1.94	0.1595	1.2646	0.7759	0.6630
" 20 " " "	37.25	2.14	9	2.96	16.5	745	1.55	0.0538	1.8588	0.2617	0.9743

From which is calculated—

	Concentration of the potash sol. Begin.	End.	Employed to 1 mol. ether molec. KOH.	Decomp. of ether in Organic Salts.	Ketone and CO_2	Total.
Propylethyl acetoacetate with 10 per cent. KOH sol.	10.00	1.43	3.06	25.78	71.68	97.46
" 20 " " " I	19.69	1.27	3.16	44.41	55.16	99.57
" 20 " " " II	19.69	1.23	3.16	47.88	49.81	97.69
Dipropylethyl acetoacetate with 10 per cent. KOH sol. I	9.91	1.03	3.00	58.49	34.29	92.78
" 10 " " " II	9.91	1.02	3.00	59.09	36.26	95.35
" 20 " " "	20.10	0.83	3.22	86.84	12.23	99.07

The following table offers a convenient comparison of the decomposition products of the mono- and dipropylethyl acetoacetates with those of the methyl and ethyl derivatives as given by Wislicenus.[1]

	Methyl.	Ethyl.	Propyl.	Dimethyl.	Diethyl.	Dipropyl.
With 10 per cent. KOH sol.						
Ketone and CO_2	86.28	91.52	71.68	91.73	54.15	34.24
Organic Salts	13.70	8.75	25.78	7.46	42.50	58.78
With 20 per cent. KOH sol.						
Ketone and CO_2	68.16	75.44	55.16	80.02	30.86	12.22
Organic Salts	31.20	23.75	44.41	19.96	69.46	86.69

From the above it is seen that monopropylethyl acetoacetate with both dilute and concentrated potash solution undergoes a decomposition by which ketone and carbon dioxide preponderate,

[1] Ann. Chem. **190**, 280.

which behavior is analogous to that of the other mono derivatives. Dipropylethyl acetoacetate, on the contrary, yields by decomposition with both dilute and concentrated alkali in a greater degree than the diethylethyl acetoacetate, principally organic salts, which behavior is especially marked when compared with the methyl derivative.

Dipropylacetic Acid.

Since it is established by the experiments just described that, by the decomposition of dipropylethyl acetoacetate with alkalies, principally organic acids are obtained, this circumstance was, therefore, taken advantage of for the preparation of dipropylacetic acid. 20 grams of dipropylethyl acetoacetate were treated on the water bath with 201 cc. of a 15 per cent. alcoholic solution of potash, with inverted condenser, and warmed for several hours. After dilution with water, the oily layer of ketone was separated, the aqueous alkaline solution was neutralized with sulphuric acid and evaporated to dryness; out of the dry residue the sodium salt of the organic acid was extracted with absolute alcohol, and in this manner purified. It forms a colorless, deliquescent mass. All attempts to obtain it in crystals were unsuccessful. By the addition of sulphuric acid to the salt the free acid was obtained, which was then dried and fractionally distilled.

The analysis yielded results in accordance with the anticipated formula $(C_3H_7)_2CH.CO.OH$.

I. 0.1238 gram acid gave 0.1269 gram H_2O; 0.3008 gram CO_2.
II. 0.1253 gram " 0.1273 gram H_2O; 0.3042 gram CO_2.

	Calculated.	Found. I.	Found. II.
C_8	66.67	66.26	66.21
H_{16}	11.11	11.39	11.29
O_2	22.22	...	...
	100.00		

Dipropylacetic acid is a colorless, oily liquid, with a slightly acid reaction, difficultly soluble in water, and possessing the characteristic odor of the higher fatty acids. Its specific gravity is 0.9215 at 0°, compared with water at 4°. It boils at 219.5°.

Silver nitrate, copper sulphate and lead acetate give with the sodium salt precipitates. The barium salt is easily soluble. The

isomeric caprylic acid, which is a solid at ordinary temperature, boils at 232°, and forms a difficultly soluble barium salt.

Ethyl Ether.—The ether was prepared by decomposition of the silver salt (11 grams) with ethyl iodide (6.21 grams). The reaction came to an end in a short time upon the water-bath. The ether was then extracted with ordinary ether, which was distilled off. The remainder was then fractionally distilled, and the following result obtained by the combustion:

0.2256 gram substance gave 0.2378 gram H_2O; 0.5723 gram CO_2.

	Calculated.	Found.
C_{10}	69.77	69.18
H_{20}	11.63	11.71
O_2	18.60	...
	100.00	

The ether is a colorless, limpid liquid of a pleasant odor, with a boiling point of 183°.

Dipropyl Acetone.

The oily layer which had separated in the saponification of dipropylethyl acetoacetate was dried with calcium chloride, fractionally distilled and analyzed.

I. 0.1733 gram substance gave 0.2009 gram H_2O; 0.4808 gram CO_2.

II. 0.1544 gram substance gave 0.1797 gram H_2O; 0.4289 gram CO_2.

	Calculated.	Found. I.	Found. II.
C_9	76.06	75.66	75.76
H_{18}	12.67	12.88	12.93
O	11.27	...	...
	100.00		

which results correspond to the formula $\left\{\begin{array}{l} CH_3 \\ CO \\ C(C_3H_7)_2H. \end{array}\right.$

Dipropyl acetone is a colorless, limpid liquid of a pleasant acetone odor. It boils at 173°–174°, and forms apparently no crystallizable compound with acid sodium sulphite.

Action of Sodium Amalgam upon Dipropylethyl Acetoacetate.

In order to obtain dipropylbetaoxybutyric acid, dipropylethyl acetoacetate was treated with sodium amalgam. A preliminary experiment proved unsuccessful. In repeating it, however, the precaution of neutralizing the free alkali, from time to time, with sulphuric acid was observed. When the reaction was completed, and the whole again neutralized, an oily liquid separated, which was recognized as dipropyl acetone. This being removed, the whole was evaporated to dryness, and repeatedly extracted with alcohol. Out of the alcoholic solution long needles crystallized, which proved to be sodium acetate. The mother-liquor was precipitated with silver nitrate. The precipitate was washed, dried and analyzed.

I. 0.2216 gram silver salt gave 0.3096 gram CO_2, 0.1212 gram H_2O, 0.0944 gram Ag.

II. 0.1215 gram silver salt gave 0.1713 gram CO_2, 0.0677 gram H_2O, 0.0520 gram Ag.

From these results the formula $C_8H_{15}AgO_2$ is deduced.

	Calculated.	Found. I.	II.
C_8	38.25	38.10	38.45
H_{15}	5.98	6.08	6.19
Ag	43.02	42.60	42.80
O_2	12.75	...	...
	100.00		

The composition of this salt shows it to be silver dipropylacetate. In order to establish more fully the fact that dipropylbetaoxybutyric acid had not been formed in the above reaction, the filtrate and washings from the silver salt were precipitated with sodium carbonate, and thus the excess of silver removed. The filtrate now obtained was evaporated and acidified with sulphuric acid, when an oily acid separated. This was removed, converted into the sodium salt, purified with alcohol, and then precipitated with silver nitrate. After washing and drying, the analysis gave the following result:

0.2605 gram gave 0.3577 gram CO_2, 0.1353 gram H_2O, 0.1088 gram Ag.

From which also the formula $C_8H_{15}AgO_2$ may be deduced.

	Calculated.	Found.
C_8	38.25	37.45
H_{15}	5.98	5.76
Ag	43.02	41.77
O_2	12.75	...
	100.00	

The silver salt of dipropylbetaoxybutyric acid $C_{10}H_{19}AgO_3$ has the percentage composition: C, 40.68 per cent.; H, 6.44 per cent.; Ag, 36.61 per cent.; O, 16.27 per cent.

Thus, apparently, none was formed by the action of sodium amalgam upon dipropylethyl acetoacetate, but the latter was, undoubtedly, completely saponified by the action of the free alkali. This reaction is especially interesting, as the diethylethyl acetoacetate can be easily converted into diethylbetaoxybutyric acid without great loss.

Action of Phosphoruspentachloride upon Sodium Diethylbetaoxybutyrate.

It has been shown by Wislicenus[1] that, heating hydracrylic acid and butaoxybutyric acid, acrylic and crotonic acids respectively are formed. Rohrbeck[2] obtained, by treating alphamethyloxybutyric acid, methylcrotonic acid. In a similar manner Schnapp[3] endeavored to obtain alphadiethylisocrotonic acid by the dry distillation of diethyloxybutyric acid thus:

$$\begin{array}{l} CH_3 \\ CH.OH \\ C(C_2H_5)_2 \\ CO.OH \end{array} - H_2O = \begin{array}{l} CH_2{=}CH \\ \qquad C(C_2H_5)_2 \\ \qquad CO.OH, \end{array}$$

but the result was not as anticipated, the only product obtained being diethylacetic acid, accompanied with a strong odor of aldehyde, the molecule having thus split up:

$$\begin{array}{l} CH_3 \\ C<^{OH}_{H} \\ C(C_2H_5)_2 \\ CO.OH \end{array} = \begin{array}{l} CH_3 \\ COH \\ \hline CH(C_2H_5)_2 \\ CO.OH. \end{array}$$

I endeavored to obtain diethylisocrotonic acid in another manner, viz., by the action of phosphorus pentachloride upon the sodium

[1] Ann. Chem. **166**, 23. Ibid. **149**, 205. Zeitsch. für Chem. 1869. 325.
[2] Ann. Chem, **188**, 229.
[3] Ann. Chem. **201**, 62.

salt of diethylbetaoxybutyric acid. The diethylbetachlorbutyric acid formed in the first phase of the reaction, it was anticipated, would lose one molecule of hydrochloric acid, and yield the desired acid, thus—

$$\begin{array}{l} CH_3 \\ CHCl \\ C(C_2H_5)_2 \\ CO.OH \end{array} - HCl = \begin{array}{l} CH_2{=}CH \\ \quad\quad C(C_2H_5)_2 \\ \quad\quad CO.OH. \end{array}$$

The sodium diethylbetaoxybutyrate was prepared as described by Schnapp by the action of sodium analgam and water upon diethylethyl acetoacetate, and corresponded in all its properties to those stated by him. In order to effect a more intimate contact of the salt with the phosphorus pentachloride, 18 grams of phosphorus oxychloride were added to 15.8 grams (1 mol.) of the sodium salt, and then 33.2 grams (2 mol.) phosphorus pentachloride were gradually added, and the whole heated on the water-bath with inverted condenser for several hours until the contents of the flask were quite liquid. The product was then poured into water. A dark oily liquid rose to the surface. This was separated, washed with water, and converted into the sodium salt by neutralizing with sodium carbonate, purified by repeatedly extracting with alcohol, and from this the silver salt was prepared. The combustion of this yielded the following results:

I. 0.2178 gram substance gave 0.2561 gram CO_2; 0.1052 gram Ag.

II. 0.2168 gram substance gave 0.2537 gram CO_2; 0.0967 gram H_2O.

III. 0.2201 gram substance gave 0.2563 gram CO_2; 0.1000 gram H_2O; 0.1067 gram Ag.

	Calculated.	Found. I.	II.	III.
C_6	32.28	32.07	31.91	31.76
H_{11}	4.93	...	4.96	5.05
Ag	48.43	48.30	...	48.48
O_2	14.36	...	...	...
	100.00			

These figures show conclusively that the acid formed in the above reaction is diethylacetic acid, which is also confirmed by the fact that its boiling point, 190°–192°, agrees exactly with that of the diethylacetic acid.

According to this then the reaction

$$\begin{array}{l}CH_3\\ CH.OH\\ C(C_2H_5)_2\\ CO.ONa\end{array} + 2PCl_5 = HCl + NaCl + 2POCl_3 + \begin{array}{l}CH_3\\ CHCl\\ C(C_2H_5)_2\\ CO.Cl\end{array}$$

had not taken place, but a splitting up of the molecule into the chloride of diethylacetic acid and a derivative of ethylidene, which latter, however, could not be isolated.

Action of Hydriodic Acid upon Diethyloxybutyric Acid.

The previous experiments having failed to lead to the desired object, the study of the action of diethylbetaoxybutyric acid toward fuming hydriodic acid was then undertaken with the supposition that, if the replacement of the hydroxyl group with hydrogen could in this manner be effected, then triethylacetic acid could be obtained, as expressed by the equation—

$$\begin{array}{l}CH_3\\ CH.OH\\ C(C_2H_5)^2\\ CO.OH\end{array} + 2HI = H_2O + I_2 + \begin{array}{l}CH_3\\ CH_2\\ C(C_2H_5)_2\\ CO.OH.\end{array}$$

13 grams of well dried sodium diethylbetaoxybutyrate were treated with six times its weight of fuming hydriodic acid in sealed tubes and maintained six hours at a temperature of 120°–125°. On opening the tubes the contents still fumed strongly, and were not under pressure. The dark liquid layer which separated was removed, washed, and the free iodine removed by treating with molecular silver. The oily liquid was dried over sulphuric acid and subjected to fractional distillation. It distilled almost completely over between 190° and 192°.

The combustion gave the following results:

0.2469 gram acid yielded 0.5602 gram CO_2 ; 0.2333 gram H_2O.

	Calculated.	Found.
C_6	62.07	61.88
H_{12}	10.34	10.50
O^2	27.59	...
	100.00	

The composition and the boiling point show clearly that again diethylacetic acid has been formed, and that a decomposition has taken place analogous to that in the action of phosphorus chloride. Notwithstanding this result, it still seemed not impro-

bable that, by the action of hydriodic acid at ordinary temperature, diethylbetaiodbutyric acid could be formed, which then by treatment with water and sodium amalgam would be converted into triethylacetic acid. In order to test the correctness of this idea 12 grams of the sodium salt were treated with 60 grams of fuming hydriodic acid in a covered beaker glass, and left to stand for several hours. It became quite warm from the reaction, and a dark liquid layer rose to the surface, which after being removed, washed and treated with molecular silver, contained not a trace of chemically combined iodine. The product had the odor of diethylacetic acid, and distilled clearly and completely between 189° and 192°, and was diethylacetic acid, as the combustion showed.

I. 0.2087 gram acid gave 0.4687 gram CO_2; 0.1947 gram H_2O.
II. 0.2000 gram " 0.4500 gram CO_2; 0.1878 gram H_2O.

	Calculated.	Found. I.	Found. II.
C_6	62.07	61.25	61.36
H_{12}	10.34	10.36	10.43
O_2	27.59	...	...
	100.00		

Action of Hydrobromic Acid upon Diethylbetaoxybutyric Acid.

The reaction with hydrobromic acid was undertaken in this case more with a view of establishing the universality of this repeated decomposition of the molecule into aldehyde and diethylacetic acids than in anticipation of a different result. For the experiment 13.3 grams of dry sodium diethylbetaoxybutyrate were treated with 40 grams of fuming hydrobromic acid, and let stand as before for several hours. The dark liquid layer which had separated was removed, washed, dried and fractionally distilled. By far the greatest portion distilled between 190° and 192°, with very slight formation of secondary products. The analysis gave the following result:

0.2342 gram acid gave 0.5294 gram CO_2; 0.2214 gram H_2O.

	Calculated.	Found.
C_6	62.07	61.65
H_{12}	10.34	10.50
O_2	27.59	...
	100.00	

(*To be continued.*)

Contributions from the Sheffield Laboratory of Yale College.

X.—ON ARSENICAL BISMUTH SUBNITRATE.

By R. H. Chittenden and S. W. Lambert.

In 1879, one of us, in conjunction with Prof. S. W. Johnson, made a toxical examination of a human body, in which the finding of arsenic was complicated by the presence of bismuth.[1] The internal organs contained 2.38 grains of arsenious oxide, while the entire muscular and bony tissue contained 2.84 grains of this poison; the distribution being quite regular, as was attested by the results of the individual analyses. The quantity of bismuth found in the stomach and spleen, calculated as $BiNO_4+H_2O$, was 5.38 grains. The quantity in the liver was a mere trace, wholly unweighable. In the trial which followed, the defense advanced the theory that the arsenic found in the exhumed remains had been absorbed from bismuth, of which the deceased had taken large quantities for medicinal purposes. The frequency with which this theory has been advanced as a plausible defense in similar cases, even when the arsenic has been found in considerable quantities, has led us to make the following experiments, with a view of ascertaining, first, the purity of bismuth subnitrate as regards this poison, and secondly, if arsenic is present, whether the poison is absorbed by the different organs and tissues of the body when repeated doses of the arsenical bismuth are taken.

I. *Examination of Bismuth Subnitrate.*

Dr. Taylor[2] quotes several cases where subnitrate of bismuth, administered in medicinal doses, has produced results directly traceable to arsenic, the presence of which was clearly shown by chemical analysis. Dr. Taylor[3] also mentions that he found arsenic "in comparatively large proportion in samples of the subnitrate, and that only two samples out of five were free from this poison." It has, however, been frequently asserted, on the other hand, that arsenic is but rarely present in bismuth, and then only in the merest trace.

[1] A report of this examination was published in this Journal, 2, 332.

[2] Treatise on Poisons, 470.

[3] *Loc. cit.*

Fourteen distinct samples[1] of bismuth were examined according to the following method: A weighed quantity of the subnitrate was heated in a porcelain caserole with a small quantity of pure sulphuric acid until the nitric acid was completely expelled. The pasty mass of sulphate was then mixed with a small quantity of water and 25 cc. of a dilute sulphuric acid (No. 2), and then fluid and precipitate were introduced into a Marsh apparatus of the form described by Chittenden and Donaldson[2] in the manner there explained. The greater part of the bismuth was washed into the apparatus by the use of acids Nos. 3 and 4,[3] frothing being prevented, when necessary, by the use of a few drops of sweet oil. When the evolution of hydrogen had wholly ceased, the mirror of metallic arsenic was weighed, the arsenic being afterwards removed from the weighed portion of the tube by volatilization.

Preliminary experiments were made to ascertain whether the presence of bismuth has any influence on the liberation of arsenic as arsenuretted hydrogen. Definite amounts of arsenious oxide were added to arsenic-free bismuth, and the mixtures, after heating with sulphuric acid, were introduced into the Marsh apparatus, with the following results:

Quantity of arsenic used.	Wt. of met. arsenic found when mixed with bismuth.	Wt. of met. arsenic found when introduced alone.	Theoretical wt. of met. arsenic.
.004 gram As_2O_3.	00290	.00300	.00303
.004 " "	.00280	.00290	.00303
.003 " "	.00210	.00225	.00227

Where the amount of bismuth taken was over five grams, there appeared to be occasionally a slight loss of arsenic, owing presumably to the mechanical hindrance caused by the presence of such a large amount of insoluble matter.

The samples of bismuth were analyzed with the following results:

[1] Obtained from various places in New York, Philadelphia and New Haven.

[2] This Journal, 2, 235.

[3] *Loc. cit.*

	Subnitrate taken.	Wt. of As found.	Quantity of As in 100 grams bism'h.	Quantity of As_2O_3 in 100 grams bism'h.
No. 1	4.5111 grams	.00040 gram	.00886 gram	.01169 gram
" 2	4.5141 "	.00035 "	.00775 "	.01023 "
" 3	4.5012 "	trace.		
" 4	4.5017 "	trace.		
" 5	4.5016 "	.00070 "	.01550 "	.02040 "
" 6	4.5010 "	.00030 "	.00660 "	.00870 "
" 7	4.5048 "	.0002 "	.00440 "	.00588 "
" 8	4.5123 "	.00015 "	.00330 "	.00435 "
" 9	4.5273 "	.00040 "	.00883 "	.01148 "
" 10	6.4208 "	.00080 "	.01234 "	.01630 "
" 11	5.1000 "	.00038 "	.00742 "	.00980 "
" 12	4.2128 "	.00020 "	.00474 "	.00626 "
" 13	2.5650[1] "	.00150 "	.05847 "	.07719 "
" 14	10.054 "	.0		
	Average of the fourteen determinations			.01302 "

The weighings were made on an exceedingly delicate balance, and several of the analyses were duplicated as follows:

No. 11:
1. 5.100 grams substance gave .00038 gram As = .0098 per cent. As_2O_3.
2. 4.020 grams substance gave .0003 gram As = .0098 per cent. As_2O_3.

No. 9:
1. 4.5273 grams substance gave .0004 gram As = .01148 per cent. As_2O_3.
2. 10 000 grams substance gave .0008 gram As = .01056 per cent. As_2O_3.
3. 4.500 grams substance gave .0005 gram As = .01475 per cent. As_2O_3.

No. 2:
1. 4.5141 grams substance gave .00035 gram As = .01023 per cent. As_2O_3.
2. 4.5022 grams substance gave .0003 gram As = .00879 per cent. As_2O_3.

These results show how far reliance is to be placed upon the weighing of such minute quantities, and indicate the differences to be expected in duplicate analyses made in this manner. In the three analyses of sample No. 9, it is to be noticed that the first and second results show a difference of only .00092 per cent. of As_2O_3, while in the second and third results, where there is a greater

[1] Basic carbonate of bismuth.

variation, the difference amounts to but .00419 per cent. As_2O_3; the average difference being much less.

It was next to be ascertained whether the metallic mirrors obtained in this manner were really arsenic, since from the usual methods of preparation of bismuth subnitrate, antimony might be present. Several of the mirrors were treated with pure and dry hydrogen sulphide gas, when, with the aid of a gentle heat, the dark metallic mirror changed to a *bright yellow* color. Again, several mirrors were treated separately with pure nitric acid. The solutions on evaporation left a small white residue, readily soluble in a drop of water. A drop of concentrated silver nitrate solution added to this residue produced a heavy brick-dust red precipitate of silver *arsenate*, readily soluble in ammonia, thus showing without doubt the presence of arsenic.

From an examination of the results obtained, it is seen that only one sample out of the fourteen analyzed is absolutely free from arsenic, while the average content of poison in the samples examined is .013 per cent., or 13 milligrams of arsenious oxide in 100 grams of bismuth. This amount is equivalent to two-tenths of a grain of arsenious oxide. In sample No. 13 the amount is not so insignificant. Here 100 grams of the basic carbonate of bismuth contain 77 milligrams of arsenious oxide, or 1.2 grains, which constitutes half a fatal dose of this poison. The subnitrate of bismuth in particular is a medicine very extensively used, and though it may not contain arsenic in sufficient quantity to be in itself productive of harm, still the presence of such a poison in so common a medicine is greatly to be deplored, from the unjust conclusions and serious mistakes it is liable to cause.

II. *Absorption of Arsenic from Bismuth Subnitrate.*

Arsenic is not strictly an accumulative poison. It accumulates for a time in certain of the organs and tissues of the body, but elimination soon commences, and if all the excretory functions are in normal condition, it is very questionable whether there can be any great retention or accumulation of the poison by the various organs of the body when very small quantities are taken at periods somewhat remote from each other. It is a very important question whether the elimination of arsenic in the living body goes on with the same degree of rapidity as its absorption. All the facts at present, how-

ever, point to a rapid and eventually a complete elimination of the poison; still there is no evidence to show that even such small quantities of arsenic as are present in these samples of bismuth may not be absorbed and give rise to an appreciable accumulation of this poison in the various organs of the body. It has therefore seemed desirable to ascertain exactly to how great an extent arsenic is absorbed and retained when arsenical bismuth is taken. A large and healthy dog was therefore selected, and a given quantity of bismuth subnitrate was administered to him three times daily with his food, in gradually increasing doses. The feeding of bismuth was commenced on the morning of March 12th, and continued without interruption until April 19th, the last dose being given at night. On April 20th, 24 hours after the last dose of bismuth was given, the dog was killed, and the various organs and a portion of the muscular tissue were preserved for analysis.

The bismuth used was sample No. 9, which contained, according to the average of the three analyses made, .01226 per cent. of arsenious oxide. The bismuth was given at first in doses of .0648 gram. On the third day .1296 gram was given, on the sixth .5184 gram three times daily. The dose was then rapidly increased, until on the 28th of March 6.48 grams were given three times a day, which dose was continued until April 19th, the end of the experiment. During the entire period of five weeks 539 grams of bismuth subnitrate were given, which quantity must have contained .06608 gram, or a little more than one grain of arsenious oxide. The amount of arsenic taken per day in the bismuth for the last three weeks was 2.38 milligrams.

The dog was apparently unaffected by the bismuth. A post mortem examination of the stomach showed the mucous membrane slightly congested in a few places. The various organs of the body were subjected individually to analysis for arsenic, and in several cases for bismuth also. The organs were examined for arsenic by the method described by Chittenden and Donaldson,[1] while for bismuth, portions of tissue were oxidized in the usual manner by hydrochloric acid and potassium chlorate according to the method of Fresenius and Babo. The results of the analyses were as follows:

[1] This Journal, **2**, 235.

	Weight of dry tissue.	Amount of metallic arsenic found.
Stomach,	250 grams	.00036 gram.
Large Intestines,	85 "	.0006 "
Small Intestines,	300 "	.0002 "
Liver,	415 "	In these organs, distinct mirrors were obtained which, though unweighable, were easily arranged in the accompanying order, as regards amount.
Spleen,	23 "	
Brain,	45 "	
Blood (not dried)	552 "	
Kidneys,	54 "	In these organs, exceedingly minute stains were obtained, too small to be identified other than as the merest brown spots.[1]
Heart,	81 "	
Lungs,	114 "	
Muscle (thigh)	216 "	

In the stomach and intestines bismuth was found in considerable quantities. In the liver and blood, on the other hand, only a very small trace was found, thus showing the difficulty with which bismuth is absorbed. From the above results we can conclude, then, that the greater part of the arsenic taken in the bismuth was not absorbed. For a period of three weeks 2.38 milligrams of arsenious oxide were taken each day. This amount if absorbed would have given a much larger content of arsenic for the various organs of the body than was found. Even supposing the rate of elimination to have been equal in this case to the rate of absorption, still then we must have found an appreciable amount of arsenic in the kidneys, since it has been clearly proven that the greater part of absorbed arsenic is eliminated by these organs. Again, the amount of arsenic found in the alimentary canal, particularly in the large intestines, was only one-half the amount contained in the last three doses of bismuth taken, a portion of which remained in the alimentary canal at the time of death. This then was not absorbed arsenic, but simply the amount contained in the bismuth still remaining in the alimentary canal. The amount found in the liver, brain and blood is, however, evidence of slight absorption.

The non-absorption of the arsenic is probably dependent upon the form in which it exists in the bismuth. If present in the form of arsenious oxide it would be readily dissolved by water. According to Taylor,[2] hot water cooling from 100° C. on arsenious oxide in powder, dissolves about the 400th part of its weight, which is approximately in the proportion of 77 milligrams of arsenious

[1] All the chemicals employed in the analyses were absolutely free from arsenic, giving no deposit whatever in the Marsh apparatus.

[2] Treatise on Poisons, 287.

oxide to 30 cc. of water. Five grams of bismuth subnitrate, sample No. 1, were treated with about 350 cc. of boiling water, which was allowed to cool on the powder with occasional agitation. When nearly cold the fluid was filtered off and the residual bismuth washed with about 250 cc. of boiling water. Filtrate and washings were then evaporated nearly to dryness on the water-bath, and the residue, dissolved in sulphuric acid No. 2, was introduced into the Marsh apparatus. Not even a trace of a mirror was obtained. Considerable bismuth had been dissolved, but no arsenic, thus apparently showing that the arsenic exists in the bismuth salt in some form other than arsenious oxide. The non-absorption of the arsenic depends then on its insolubility. The arsenic is however completely dissolved by dilute sulphuric acid; thus 10 grams of bismuth subnitrate, sample No. 9, were dissolved in a moderate quantity of dilute sulphuric acid, from which the bismuth separated again almost immediately as crystalline bismuth sulphate. By washing this precipitate with an abundance of water the arsenic was wholly removed from the bismuth, and by introducing the evaporated filtrate and washings into the Marsh apparatus the entire amount of arsenic was obtained. We can then conclude from our experiments that while medicinal bismuth subnitrate contains a weighable quantity of arsenic, the poison is not present in the samples which we have experimented with, in a form capable of being readily absorbed into the system. This fact however does not diminish the need for a preparation of bismuth entirely free from arsenic.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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(Continued from p. 332.)

Five to One Series.—Salts of this series were discovered at an early period in the history of the subject by Zenker.[1] The ammonium salt was analyzed by Zenker[2] and Werncke,[3] and recently

[1]Journal für prakt. Chemie, **58**, 256. [2] *Loc. cit.* [3] Zeitschrift für analyt. Chemie, **14**, 12.

by Rammelsberg.[1] Debray obtained the same salt, but has published no analyses. Rammelsberg also obtained the corresponding potassium salt, as well as an acid salt of the same series. The alkaline salts are colorless, and separate in well-defined crystals, which are usually easily soluble in water. The acid of the series, as Debray has stated, cannot be obtained by the decomposition of its salts, being resolved by acids into free phosphoric acid and salts of the 24-atom series. The decomposition may probably be expressed by the equation

$$24(5MoO_3.P_2O_5.3H_2O) = 5(24MoO_3.P_2O_5.3H_2O) + 19(P_2O_5.3H_2O).$$

All the neutral salts are tribasic (old style), or more correctly hexatomic, but well-defined acid salts exist in which the ratio of the molybdic oxide to the fixed base is as 10 : 5. Such salts have been obtained by Rammelsberg and by myself. The salts of the higher series are decomposed by alkalies, as stated by Debray, salts of the 5-atom series and alkaline molybdates being formed. Conversely, when a mineral acid is added to a solution of an alkaline salt of the 5-atom series, a salt of a higher series is formed, frequently as a yellow crystalline precipitate. The neutral salts of this series hitherto described have respectively the formulas

$$5MoO_3.P_2O_5.3K_2O + 7aq.$$
$$5MoO_3.P_2O_5.3(NH_4)_2O + 7aq.$$
$$5MoO_3.P_2O_5.3Na_2O + 14aq.$$
$$5MoO_3.P_2O_5.3Ag_2O + 7aq.$$

5 : 3 *Phospho-molybdate of Ammonium.*—This beautiful salt appears, as already stated, to have been first obtained by Zenker. It is readily obtained by dissolving together five molecules of ammonic molybdate and two of ammonic phosphate, and evaporating the solution, when beautiful prismatic crystals, with a glassy lustre, separate. These may easily be purified by recrystallization. The salt is readily soluble in hot, less easily in cold water. The solution has an acid reaction. Zenker's analyses, as well as those of Werncke, agree closely with the formula

$$5MoO_3.P_2O_5.3(NH_4)_2O + 7aq,$$

[1] *Loc. cit.*

in which formula the phospho-molybdic acid is regarded as tribasic. Debray gives the same formula, without details of analysis, and Rammelsberg has very recently again analyzed the salt, confirming the results of Zenker. The salt in question is particularly interesting, first, because the number of atoms of molybdic oxide is *uneven*; and secondly, because the basicity of the acid appears to be 3, and not 6, even when the salt has separated from neutral solutions.

Jörgensen[1] has described two well-defined crystalline salts belonging to this series, and having according to his notation respectively the formulas

$$Co_2(NH_3)_{10}Cl_2.(5MoO_3.2PO_4H)$$

and

$$Co_2(NH_3)_{10}Cl_2.(5MoO_3.2PO_4NH_4).$$

I should write these

$$5MoO_3.P_2O_5.Co_2(NH_3)_{10}Cl_2O_2.H_2O$$

and

$$5MoO_3.P_2O_5.Co_2(NH_3)_{10}Cl_2O_2(NH_4)_2O.$$

It will readily be seen that both salts correspond to the acid represented by the formula

$$5MoO_3.P_2O_5.H_2O.$$

Acid 10 : 5 *Ammonium Salt.*—When ammonic phosphate is dissolved in boiling water, and molybdic oxide is added in small portions at a time, the oxide readily dissolves, but a greater or less quantity of a white insoluble crystalline salt is formed. The filtrate deposits on evaporation large colorless crystals, which appear to be either trimetric or monoclinic. Of these crystals,—

1.1126 gram lost on ignition with WO_4Na_2 0.2076 gram = 18.66 per cent. NH_3 and H_2O.

1.2962 gram lost on ignition with WO_4Na_2 0.2425 gram = 18.71 per cent. NH_3 and H_2O.

1.2165 gram lost on ignition with WO_4Na_2 0.2247 gram = 18.47 per cent. NH_3 and H_2O.

0.9263 gram gave 0.1912 gram $P_2O_7Mg_2$ = 13.20 per cent. P_2O_5.

1.0540 gram gave 0.2196 gram $P_2O_7Mg_2$ = 13.32 per cent. P_2O_5.

[1]Journal für prakt. Chemie, [2] **18**, 209.

1.1824 gram gave 0.3018 gram $NH_4Cl = 12.41$ per cent. $(NH_4)_2O$.

1.0183 gram gave 0.2563 gram $NH_4Cl = 12.23$ per cent. $(NH_4)_2O$.

1.6430 gram gave 0.4168 gram $NH_4Cl = 12.32$ per cent. $(NH_4)_2O$.

The analyses lead to the formula

$$10MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+6aq,$$

or

$$5MoO_3.P_2O_5.3(NH_4)_2O+5MoO_3.P_2O_5.2(NH_4)_2O.H_2O+6aq,$$

which requires:

		Calc'd.	Mean.			
$10MoO_3$	1440	68.24	68.13	...	...	...
$2P_2O_5$	284	13.46	13.26	13.20	13.32	...
$5(NH_4)_2O$	260	12.32	12.32	12.41	12.23	12.32
$7H_2O$	126	5.98	6.29	6.15	6.34	6.39
	2110	100.00				

The phosphoric oxide was determined by double precipitation only, without subsequent treatment with ammonic sulphide. The percentage is a little lower than that required by the formula, which is unusual; but the general agreement of the analyses with the formula is satisfactory. Rammelsberg has described an acid potassium salt with the formula

$$10MoO_3.P_2O_5.5K_2O.H_2O+19aq.$$

It is therefore at least probable that we shall find another ammonia salt with 20 atoms of water, and another potassium salt with 7 atoms. Zenker has described another potassic salt to which he gives the formula,—as I should write it,—

$$9MoO_3.P_2O_5.4K_2O.2H_2O+18aq;$$

but the results of his analyses differ very widely from the percentages required by the formula, and on repeating his process I obtained only the 10:5 atom salt of Rammelsberg. The formula given above for this salt requires 11.11 per cent. P_2O_5. I found 11.22 per cent.

Rammelsberg[1] has also described a white insoluble potassium salt to which he gives the formula $15MoO_3.P_2O_5.5K_2O$, but without any statement of his analyses.

[1] *Loc. cit.*

ARSENIO-MOLYBDATES.

Compounds of arsenic and molybdic oxides have been described by Seyberth[1] and by Debray.[2] Seyberth obtained an acid with the formula,—as I should write it,—

$$7MoO_3.As_2O_5.3H_2O+11aq,$$

and the three corresponding salts:

$$7MoO_3.As_2O_5.(NH_4)_2O.2H_2O+4H_2O$$
$$7MoO_3.As_2O_5.3BaO$$
$$7MoO_3.As_2O_5.3Ag_2O.$$

Debray obtained the acids and one or two salts of two different series, which may be represented respectively by the formulas:

$$20MoO_3.As_2O_5.3H_2O+24aq$$
$$20MoO_3.As_2O_5.3K_2O$$
$$20MoO_3.As_2O_5.3(NH_4)_2O$$
$$6MoO_3.As_2O_5.3H_2O+13aq$$
$$6MoO_3.As_2O_5.4(NH_4)_2O+aq$$
$$6MoO_3.As_2O_5.(NH_4)_2O+4aq$$
$$6MoO_3.As_2O_5.NaO_2+12aq.$$

Debray considers the formula of the 20-atom ammonium salt as probable only, and regards the water determination in the corresponding acid as not quite certain. Neither Seyberth nor Debray has described the analytical methods employed, or given the details of the analyses.

I have found it most advantageous to separate arsenic from molybdic oxide by precipitating with magnesia mixture, redissolving the ammonio-magnesic arsenate, and precipitating a second time with ammonia after adding a little magnesia mixture. The ammonio-magnesic arsenate may be digested with ammonic sulphide without decomposition; but after the second precipitation it does not retain molybdic oxide, and the subsequent treatment is therefore unnecessary. To determine the sum of the molybdic and arsenic oxides I precipitate the two together with mercurous nitrate and mercuric oxide, in the manner already described for the estimation of molybdic and phosphoric oxides, filter upon paper, and after drying roll up the filter and its contents and ignite cautiously

[1] Berichte der deutsch. chem. Gesellschaft, 1874, 391. [2] Comptes Rendus, 78, 1408.

in a porcelain crucible. By slow and careful heating the filter may be completely burned without loss of molybdic or arsenic oxides, this result being attained by the oxygen of the mercurous and mercuric oxides present. A weighed quantity of sodic tungstate is then to be added in fine powder, the mass well mixed in the crucible, and then cautiously heated until mercury is completely expelled, and after cooling a white fused mass remains. A second or even a third heating is necessary to insure a perfectly constant weight. The difference between the percentage of arsenic oxide, As_2O_5, and the sum of the percentages of the arsenic and molybdic oxides, gives the percentages of molybdic oxide with a very fair degree of approximation. In these salts the water must always be determined by ignition with sodic tungstate or some similar compound, since both arsenic and molybdic oxides are volatile.

Sixteen to one Series.—When solutions of ammonic arsenate and acid molybdate (7 : 3 salt) are mixed, a beautiful white crystalline precipitate is thrown down, which is very insoluble in cold water, but dissolves slightly in boiling water, giving, however, a turbid solution. The salt is readily soluble in ammonia water. The portion analyzed was well washed on a filter with cold water and dried on woollen paper. In this salt,—

1.1322 gram lost on ignition with WO_4Na_2 0.1636 gram NH_3 and $H_2O = 14.45$ per cent.

1.3389 gram gave 0.2481 gram $NH_4Cl = 9.00$ per cent. $(NH_4)_2O$.

1.4276 gram gave 0.1478 gram $As_2O_7Mg_2 = 7.68$ per cent. As_2O_5.

The analyses lead to the formula

$$16MoO_3.As_2O_5.5(NH_4)_2O.H_2O + 8aq.$$

which requires :

		Calc'd.			
$16MoO_3$	2304	77.94	85.72	77.97	85.65
As_2O_5	230	7.78		7.68	
$5(NH_4)_2O$	260	8.79	14.28	9.00	14.45
$9H_2O$	162	5.49		5.45	
	2956				

The salt may have lost a little ammonia in drying. When potassic arsenate and acid molybdate are mixed, a similar salt is formed. A solution of arsenic acid gives at once in solutions of

acid ammonic or potassic molybdate a beautiful white crystalline precipitate, insoluble in cold water, but soluble in a large quantity of boiling water, forming cloudy solutions which pass freely through a filter. These may serve as starting-points for new investigations. The arsenio-molybdate above described is not perceptibly altered by long boiling with nitric acid, but the existence of higher compounds containing 22 or 24 molecules of molybdic to one of arsenic oxide appears at least extremely probable.

The phospho-molybdates and arsenio-molybdates now known with some degree of certainty are as follows:

$24MoO_3.P_2O_5.6H_2O+47aq$	$Mo_{24}P_2O_{71}(HO)_{12}+47aq$
$24MoO_3.P_2O_5.6H_2O+43aq$	$Mo_{24}P_2O_{71}(HO)_{12}+43aq$
$24MoO_3.P_2O_5.6H_2O+24aq$	$Mo_{24}P_2O_{71}(HO)_{12}+24aq$
$24MoO_3.P_2O_5.2K_2O.4H_2O$	$Mo_{24}P_2O_{71}(KO)_4(HO)_8$
$24MoO_3.P_2O_5.CeO.5H_2O+18aq$	$Mo_{24}P_2O_{71}(CeO_2)(HO)_{10}+18aq$
$48MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+16aq$	$Mo_{48}P_4O_{148}(NH_4O)_{10}(HO)_2+16aq$
$22MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+9aq$	$Mo_{22}P_2O_{66}(NH_4O)_6(HO)_6+9aq$
$22MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+6aq$	$Mo_{22}P_2O_{65}(NH_4O)_6(HO)_6+6aq$
$22MoO_3.P_2O_5.3(NH_4)_2O$	$Mo_{22}P_2O_{68}(NH_4O)_6$
$22MoO_3.P_2O_5.3K_2O.3H_2O+9aq$	$Mo_{22}P_2O_{65}(KO)_6(HO)_6+9aq$
$22MoO_3.P_2O_5.7Ag_2O+14aq$	$Mo_{22}P_2O_{64}(AgO)_{14}+14aq$
$44MoO_3.2P_2O_5.5K_2O.H_2O+21aq$	$Mo_{44}P_4O_{136}(KO)_{10}(HO)_2+21aq$
$60MoO_3.3P_2O_5.8(NH_4)_2O.H_2O+11aq$	$Mo_{60}P_6O_{186}(NH_4O)_{16}(HO)_2+11aq$
$18MoO_3.P_2O_5.Na_2O.5H_2O+m aq$	$Mo_{18}P_2O_{53}(NaO)_3(HO)_{10}+m aq$
$18MoO_3.P_2O_5.2Na_2O.4H_2O+n aq$	$Mo_{18}P_2O_{54}(NaO)_4(HO)_8+n aq$
$16MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+11aq$	$Mo_{16}P_2O_{47}(NH_4O)_6(HO)_6+11aq$
$5MoO_3.P_2O_5.3Na_2O.3H_2O+11aq$	$Mo_5P_2O_{14}(NaO)_6(HO_6)+11aq$
$5MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+4aq$	$Mo_5P_2O_{14}(NH_4O)_6(HO)_6+4aq$
$5MoO_3.P_2O_5.3K_2O.3H_2O+4aq$	$Mo_5P_2O_{14}(KO)_6(HO)_6+4aq$
$5MoO_3.P_2O_5.3Ag_2O.3H_2O+4aq$	$Mo_5P_2O_{14}(AgO)_6(HO)_6+4aq$
$10MoO_3.2P_2O_5.K_2O.H_2O+19aq$	$Mo_{10}P_4O_{34}(KO)_{10}(HO)_2+19aq$
$10MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+6aq$	$Mo_{10}P_4O_{34}(NH_4O)_{10}(HO)_2+6aq$
$20MoO_3.As_2O_5.6H_2O+21aq$	$Mo_{20}As_2O_{59}(HO)_{12}+21aq$
$20MoO_3.As_2O_5.3K_2O$	$Mo_{20}As_2O_{62}(KO)_6$
$20MoO_3.As_2O_5.3(NH_4)_2O$	$Mo_{20}As_2O_{62}(NH_4O)_6$
$16MoO_3.As_2O_5.5(NH_4)_2O.H_2O+8aq$	$Mo_{16}As_2O_{47}(NH_4O)_{10}(HO)_2+8aq$

$7MoO_3.As_2O_5.6H_2O+aq$	$Mo_7As_2O_{20}(HO)_{12}+8aq$
$7MoO_3.As_2O_5.(NH_4)_2O.5H_2O$	$Mo_7As_2O_{20}(NH_4O)_2(HO)_{10}$
$7MoO_3.As_2O_5.3BaO$	$Mo_7As_2O_{23}(BaO_2)_3$
$7MoO_3.As_2O_5.3Ag_2O$	$Mo_7As_2O_{23}(AgO)_6$
$6MoO_3.As_2O_5.6H_2O+10aq$	$Mo_6As_2O_{17}(HO)_{12}+10aq$
$6MoO_3.As_2O_5.4(NH_4)_2O+aq$	$Mo_6As_2O_{19}(NH_4O)_8$
$6MoO_3.As_2O_5.(NH_4)_2O.2H_2O+aq$	$Mo_6As_2O_{20}(NH_4O)_2(HO)_4+2aq$
$6MoO_3.As_2O_5.Na_2O.5H_2O+7aq$	$Mo_6As_2O_{17}(NaO)_2(HO)_{10}+7aq$

For the convenience of comparison with the corresponding compounds of tungsten, I have in writing these formulas as far as possible assumed that all the phospho-molybdic and arsenio-molybdic acids contain 12 atoms of hydroxyl, or, in the language appropriate to the old notation, are six-basic. With the material before us, we are now prepared to discuss the question of the basicity of the phospho-tungstates and phospho-molybdates as well as of the corresponding arsenic compounds.

The general results to which the study of the phospho-molybdates and arsenio-molybdates has led are as follows:

1. The phospho-molybdates form a series of which the lowest term contains five atoms of molybdic to one of phosphoric oxide, and the highest twenty-four atoms of the former to one of the latter.

2. As in the case of the phospho-tungstates, the greater number of the molybdenum compounds contain an even number of atoms of tungstic acid. The homologizing term is therefore $2MoO_3$ for these cases.

3. By far the greater number of phospho-molybdates contain *three* atoms of fixed base (old style), or, in more modern language, may be considered as derived from acids containing *six* atoms of hydroxyl. Anhydrous compounds of this type occur, and are not always simply residues obtained by heating salts which may be considered as acid, as containing, for example, $3R_2O.3H_2O$. It seems therefore necessary to admit the existence of acids of the general type

$$nMoO_3.P_2O_5.3H_2O,$$

which may, however, stand in the relation of pyro-acids to other acids of the type

$$nMoO_3.P_2O_5.6H_2O.$$

4. On the other hand, while no single phospho-molybdate containing more than three atoms of fixed base for one of phosphoric

oxide has been obtained in a state of indubitable purity, it is probable that there is at least one salt with *six* or more atoms of fixed base. I refer to the silver salt which I have expressed by the formula

$$22MoO_3.P_2O_5.7Ag_2O+14aq.$$

5. Setting aside the evidence derived from the analogy of the phospho-molybdates and phospho-tungstates, there is at present no sufficient proof of the existence of a series of phospho-molybdates or arsenio-molybdates containing more than *three* atoms of fixed base. Such purely negative evidence must not be too highly regarded.

6. As in the case of the phospho-tungstates, there exists a class of phospho-molybdates in which the ratio of the number of atoms of base to that of the number of atoms of phosphoric oxide is as 5:2, the number of atoms of molybdic oxide being even.

Since the publication of my work on the phospho-tungstates and arsenio-tungstates, a paper by Sprenger[1] on the phospho-tungstates has appeared. Sprenger has examined, with a single exception, only the compounds of the 24:1 series, and has added a number of new salts, which, so far as regards their constitution, fully confirm my own results. The compounds described, belonging to the 24-atom series, are the following:

$$24WO_3.P_2O_5.3H_2O+58aq$$
$$24WO_3.P_2O_5.3BaO+58aq$$
$$24WO_3.P_2O_5.2BaO.H_2O+58aq$$
$$24WO_3.P_2O_5.BaO.2H_2O+58aq$$
$$24WO_3.P_2O_5.3Cu_2O+58aq$$
$$24WO_3.P_2O_5.3Ag_2O+58aq$$
$$24WO_3.P_2O_5.2Ag_2O.H_2O+58aq.$$

Sprenger's formula for the octahedral acid agrees with that which I had given if we consider the acid as tribasic. The other salts which he has described are new, and form a valuable addition to our knowledge of this class of compounds. It is well worthy of notice, that in all of his salts, the acid included, the number of atoms of water is the same. The acid with 58 atoms of water of crystallization forms, therefore, a complete and stable molecular structure in which 2, 4, or 6 atoms of hydrogen are replaceable. I do not recall any other series in which this constancy of crystalline water occurs,

[1] Journal für prakt. Chemie, **22**, 418.

at least to the same extent. Sprenger has also obtained a salt of the 22-atom series which is of much interest. This is the barium salt,

$$22WO_3.P_2O_5.7BaO+59\frac{1}{2}aq,$$

and its special interest depends upon the fact, first, that the ratio of the tungstic to the phosphoric oxide is as 22 : 1, and, secondly, that the salt contains *seven* atoms of fixed base, or, in other words, must be considered as derived from an acid containing at least *fourteen* atoms of hydroxyl. Sprenger asserts that he has obtained the corresponding acid, and it is to be hoped that he will pursue the subject farther. This barium compound furnishes additional evidence of the independent existence of a series in which the ratio is 22 : 1, and in addition it renders more probable the formula which I have given for Debray's silver salt,

$$22MoO_3.P_2O_5.7Ag_2+14aq.$$

From these two tolerably well-established cases it would appear that we are not justified in holding that the phospho-tungstates, phospho-molybdates, and corresponding arsenic compounds, have a basicity of which the higher limit is six. I may here mention that I shall hereafter describe a vanadio-molybdate of ammonium, the analyses of which agree well with the formula

$$18MoO_3.V_2O_5.8(NH_4)_2O+15aq.$$

The risk of drawing hasty conclusions from purely negative evidence is particularly great in discussing the degree of basicity of this whole class of compounds, but I shall endeavor to show that it is possible to devise structural formulas which will embrace and explain all degrees of basicity which appear to be possible under the general conditions of the problem.

We may, as in the case of the alkaline tungstates already discussed, assume that both tungsten and molybdenum are hexatomic, and, as in that case, we may start from the commonly received formula for potassic dichromate,

$$\begin{array}{l} CrO_2-O-K \\ \quad | \\ \quad O \\ \quad | \\ CrO_2-O-K \end{array}$$

which may be equally well applied to hexatomic tungsten,

$$\begin{array}{ccccccc}
 & & O & & & & \\
 & & \| & & & & \\
O & = & W & - & O & - & K \\
 & & | & & & & \\
 & & O & & & & \\
 & & | & & & & \\
O & = & W & - & O & - & K \\
 & & \| & & & & \\
 & & O & & & &
\end{array}$$

If we further suppose that the separate terms of the structural formulas are symmetrically arranged, and take a 6 : 1 phosphotungstate

$$6WO_3.P_2O_5.6H_2O \qquad \text{or} \qquad 6WO_2.P_2O_5.(HO)_{12}$$

as an illustration, we may, with at least a certain degree of probability, express the structure as follows:

$$\begin{array}{ccccccc}
HO & - & WO_2 & = & WO_2 & - & OH \\
 & & | & & | & & \\
HO & - & WO_2 & - & WO_2 & - & OH \\
 & & | & & | & & \\
HO & - & WO_2 & - & WO_2 & - & OH \\
 & & | & & | & & \\
 & & O & & O & & \\
 & & | & & | & & \\
3(HO) \equiv & & PO & - O - & OP & & \equiv (OH)_3
\end{array}$$

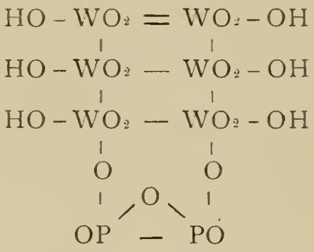
This formula explains the basicity of the acid satisfactorily. It also shows that, as six atoms of hydroxyl are united with phosphorus, and six with tungstic oxide, there should be theoretically a limiting case corresponding to an acid containing six atoms of hydroxyl, and represented by the formula

$$6WO_3.P_2O_5.3H_2O \qquad \text{or} \qquad 6WO_2.O_3.P_2O_5.(HO)_6$$

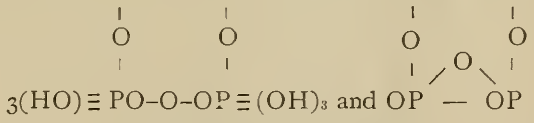
and structurally by

$$\begin{array}{ccccc}
WO_2 & & = & & WO_2 \\
| & \diagdown & O & \diagup & | \\
WO_2 & - & O & - & WO_2 \\
\| & & & & \| \\
WO_2 & - & O & - & WO_2 \\
| & & & & | \\
O & & & & O \\
| & & & & | \\
3(HO) \equiv PO & - & O & - & OP \equiv (OH)_3.
\end{array}$$

According to this view six atoms of hydroxyl are always associated with phosphorus, or, as the case may be, with arsenic. I consider this view of the subject by far the more probable. At the same time, however, it is also possible that we may have the structural formula,



in which all the atoms of hydroxyl are associated directly with tungsten, and in the present state of our knowledge we can only decide the question upon general grounds of probability, so that our conclusions are at best uncertain. Finally, both formulas being at least possible, it may be that there are two isomeric modifications of each series of acids represented respectively by the formulas above given. There is no present evidence of the existence of such isomeric modifications in the case of phospho-tungstates, phospho-molybdates, or the corresponding arsenic series; but Marignac has shown that there are two isomeric series of silico-tungstates, which he calls respectively silico-tungstates and tungsto-silicates, and it may be that the difference between these depends upon differences in the mode of combination, precisely similar to those which I have pointed out above. I shall return to this subject in the general discussion of my results. With respect to the two linking terms,

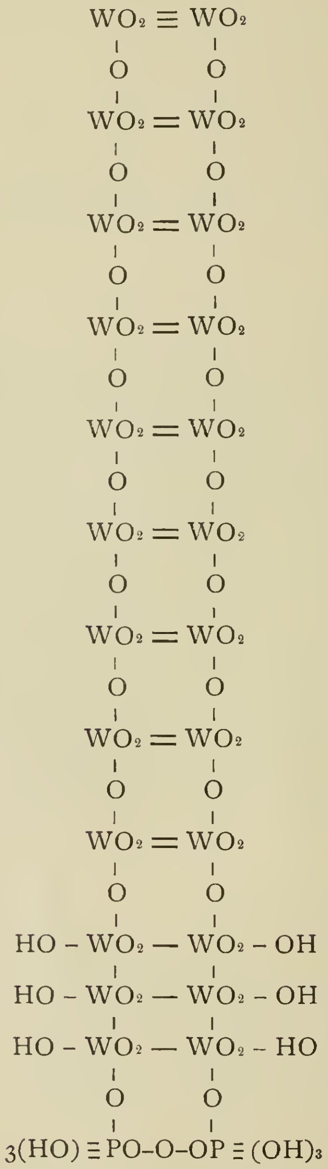


no assumption is made which is not in perfect accordance with commonly accepted views of the subject.

We may now consider the most general case, that, namely, in which there are twenty-four atoms of tungstic or molybdic to one of phosphoric or arsenic oxide. We have for an acid of this type

$$24WO_3.P_2O_5.6H_2O \quad \text{or} \quad 24WO_2.O_{18}.P_2O_5.(HO)_{12}$$

and in accordance with the principles above laid down the structural formula may be written:



The case of an acid containing for twenty-four atoms of tungstic oxide six atoms of hydroxyl may easily be deduced from the above, upon the principle explained in the first example cited. Without again writing the cumbrous formula, it may easily be seen that the cases of acids containing more than twelve atoms of hydroxyl, if such really exist, are embraced in the above given structural formula; and that in such cases there will be two variations in the mode of combination of the hydroxyl, similar to the two which occur when there are six or twelve atoms of hydroxyl. The structural formula given would explain simply and naturally the *tribasic* character of all known phospho-molybdates and phospho-tungstates containing twenty-four atoms of metallic oxide, since in these all the hydroxyl may be united with phosphorus exclusively, or with tungsten exclusively. It only remains to consider the case of the compounds having for one atom of phosphoric or arsenic oxide an *uneven* number of atoms of metallic oxide, as, for instance, the 5 : 1 and 7 : 1 series. In these cases also there exists, as has been shown, a second and derived series, of which the successive terms are to be regarded as formed from those of the first series by doubling the molecular weight and dropping an atom of fixed base. Thus, we have

$5MoO_3.P_2O_5.3H_2O$	and	$10MoO_3.2P_2O_5.5K_2O.H_2O+19aq$
$7MoO_3.As_2O_5.3H_2O$		$14WO_3.2P_2O_5.5Na_2O.H_2O+42aq$
$22MoO_3.P_2O_5.3H_2O$		$44MoO_3.2P_2O_5.5K_2O.H_2O+21aq$
$24MoO_3.P_2O_5.3H_2O$		$48MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+16aq$

All these salts appear to have an acid reaction. They may all be regarded as acid six-basic salts, and it is easy to see that the two series may be reduced to one by doubling the formulas of all the terms on the left, so that we shall have a single series, of which the successive terms are

$$10MoO_3.2P_2O_5.6H_2O$$
$$12MoO_3.2As_2O_5.6H_2O$$
$$14WO_3.2P_2O_5.6H_2O$$
$$\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot$$
$$48MoO_3.2P_2O_5.6H_2O$$

This view in nowise excludes acids or salts of a higher degree of basicity. It has the advantage of bringing all the compounds together, and of being more completely in accordance with what

we know of the constitution of salts belonging to simpler types. The structural formulas which I have given—provisionally, of course—may easily be modified to suit this view, and will all be symmetrical and suggestive of various possible isomerisms.

The study of other complex inorganic acids will, doubtless, throw further light upon the subject, and to it I shall continue to devote my leisure. It already begins to appear that inorganic compounds may possess an unexpected degree of complexity, and that very wide fields of research in inorganic chemistry are still open.

(*To be continued.*)

THE QUANTITATIVE SEPARATION OF ROSIN FROM FATS.

By Thomas S. Gladding.

The need of an accurate process for the separation of rosin from the fats and its quantitative estimation has long been felt. To meet this need numerous methods have been proposed. Thus in Prescott's "Proximate Organic Analysis," p. 90, are recommended two, the first dependent on the treatment of the fat acids containing the rosin, with petroleum naphtha; the second, on the treatment of the same with a mixture of water and a nearly equal volume of alcohol. I have given these plans a careful trial, using for the purpose a mixture of known amounts of pure fat and pure rosin, but have found them wholly unreliable, as they fail to give even an approximate determination of the rosin known to be present.

A later and better method is found in "Spons' Encyclopedia," p. 1469, in which the rosin and fats are brought into the form of neutral soda salts. After a careful drying by evaporation mixed with sand, these are digested in a mixture of absolute alcohol and ether, by which the resinate of soda is dissolved. But this method is very laborious, requiring at a later stage the use of a polariscope, and even then giving a result several per cent. from perfect accuracy, especially when the amount of rosin present is small.

The difficulty underlying the problem is the great similarity as regards solubility between oleic acid or its salts and the resins.

Every solvent for the one in the above schemes is to a considerable degree a solvent for the other. A systematic search has therefore been made for such a salt and such a solvent as shall serve to distinctly separate these two substances.

A plan of separation analogous to the separation of oleic acid from stearic and palmitic acids by digesting their lead salts in ether, thereby dissolving out the oleate of lead, has been investigated, and found to be entirely satisfactory both as regards accuracy and ease of execution.

The fatty salts of silver were found to be almost perfectly insoluble in ether, while the resinate of silver was found to be readily and abundantly soluble therein. A small percentage of alcohol does not affect the solubility of either, and for the sake of an advantage gained thereby was used in the course of experiments undertaken.

In applying this principle of separation, the silver salts of the three acids were at first precipitated from a perfectly neutral water solution of the potash salts by a neutral solution of silver nitrate. But the difficulty attending the filtering and washing of this precipitate, and the somewhat inaccurate results obtained, which were attributed partly to the decomposition of the silver salts from exposure during drying preparatory to treating with ether, caused its abandonment.

The following plan was finally adopted with success.

About 0.5 gram of the fat acids containing the rosin is introduced into a small flask. Twenty cubic centimetres of 95 per cent. alcohol are added, and the flask rotated till the fat acids and the rosin are dissolved. A drop of phenol phthalein is now added, and then a saturated solution of caustic potash in alcohol drop by drop, with thorough agitation after the addition of each drop, until the deep red color characteristic of alkalinity is obtained. One or two additional drops are now added, and the flask placed on a water-oven and kept at the temperature of boiling alcohol for ten minutes to ensure the saponification of the last portions of fat. The flask should be loosely corked. It is now cooled and the contents washed into a graduated 100 cc. cylinder by means of concentrated ether. The cylinder is filled with the ether exactly to the 100 cc. mark; then corked, best by a common cork twisted tightly in, and the contents mixed by a moment's shaking. About one gram of C. P. *neutral* silver nitrate is now rubbed to an impalpable powder in

a small mortar and then introduced into the cylinder. The latter is vigorously shaken for ten or fifteen minutes until the flocculent precipitate of silver stearate and oleate collects in the same manner as silver chloride upon shaking, and settles clear. Fifty to seventy cc. of the supernatant liquid are now syphoned off by means of a slender syphon, previously filled with ether, into a second 100 cc. cylinder, passing the liquid through a small filter paper if it is not perfectly clear. A small quantity of pulverized silver nitrate is shaken up with this to make certain that all the oleate and stearate are precipitated. If no flocculent precipitate appears this is the case. Twenty cc. of a mixture of hydrochloric acid and water, one-third the former and two-thirds the latter, are now added, and the cylinder vigorously shaken until the decomposition of all the silver salt present is complete. After the silver chloride has settled, an aliquot portion of the supernatant ether solution is syphoned off into a platinum dish and evaporated on the top of a water-oven to dryness. The residue is rosin containing a small amount of oleic acid, which can be accurately allowed for.

The following experiments will show the allowance to be made for the oleate of silver retained in solution, as well as the reliance which can be placed upon the process for accuracy.

Exp. I. One-half a gram of pure fat acid was treated according to the above plan, but with one-half the amount of alcohol and ether.

Forty cc. shaken with HCl and evaporated gave 0.0095 gram of residue. 10 cc. contain 0.00237 gram of oleic acid.

Exp. II. One-half a gram of pure fat acid was treated in the same way with full quantities of liquid.

Eighty cc. shaken with HCl and evaporated gave 0.0188 gram of residue; 10 cc. contain therefore 0.00235 gram of oleic acid. This very small and accurate correction of 0.00235 gram for every 10 cc. of liquid shaken up with HCl was applied in the subsequent experiments.

Exp. III. Some pure white castile soap was decomposed by acid. One-half a gram of the fat acids from the soap was added to 0.050 gram of common yellow rosin (colophony) and the whole treated as above. After corrections, 0.0497 gram on the whole quantity taken was obtained instead of 0.050 gram.

In order to ascertain whether the process would succeed with linseed oil, in which rosin is often to be determined, and also to test

the process when very small quantities of rosin are present, the following experiment was made.

Exp. IV. One-half a gram of the fat acids from linseed oil was added to 0.050 gram of rosin and treated as the above.

Seventy cc. shaken with HCl · gave 0.0517 gram of residue. Subtracting the allowance for 70 cc., namely, 0.0164 gram, leaves 0.0353 gram or 0.0504 gram of rosin on the whole quantity taken instead of 0.050 gram taken.

As the principal value of the above process will be found in the estimation of rosin in soaps, of which it forms so frequent an adulterant, a number of experiments were made according to the above plan on the soap itself, dispensing with the preliminary decomposition of the soap in order to obtain the fat acids.

One gram of the soap in thin shavings is dissolved in the alcohol and treated in every way as above. Particular care is paid to the saponification as above directed, in order to make certain that no trace of unsaponified fat is left. This would pass through the remaining stages unchanged and increase the percentage of rosin. The results are so good and the process is so much simplified that this plan is recommended for commercial analysis. The determination of the percentage of fat acids is thereby avoided, and the time required for the process is shortened to a few hours. Pure soap free from rosin was used.

	Soap taken.	Rosin added.	Rosin found after correction.
Exp. V.	0.250 gram	0.0200 gram	0.0197 gram
Exp. VI.	1.000 "	0.0200 "	0.0209 "

Some experiments made by filtering the whole of the liquid instead of taking an aliquot portion as above did not give as accurate results, both on account of the difficulty of perfectly washing the flocculent precipitate, and the lesser degree of accuracy in making allowance for the oleate of silver dissolved.

Duplicate analyses of a cheap yellow soap known to contain rosin gave 29.00 per cent. and 29.30 per cent. of rosin present.

Some experiments to determine the applicability of the above process to the estimation of mineral oils and paraffin in the other fatty oils are contemplated, also a preliminary trial of a similar method of separating oleic acid from the other fat acids gives promise of accomplishing this with great accuracy.

Laboratory of Stillwell & Gladding, New York.

A NEW MANGANESE MINERAL.

By Malvern W. Iles.

In describing this mineral I have thought best to use the same general scheme of arrangement as that adopted in Dana's Mineralogy.

1. *Crystalline form.* The mineral is composed of loosely-adhering, very friable, thick orthorhombic (?) prisms, which are frequently found terminating in truncated pyramids.

2. *Hardness, etc.* (*a*) The mineral has a hardness of 0.75 to 1.0.

(*b*) The Jolly spring balance was used to determine the density. Great care was taken to obtain a very pure specimen, and sufficiently large for accuracy. The mineral was weighed in clear petroleum the density of which was 0.7975. The specific gravity was found to be 2.1627.

(*c*) Lustre: slightly glimmering, resembling pure kaolin, and a number of white efflorescent salts.

(*e*) Color: pure milky white, but sometimes stained with sesquioxide of iron.

3. *Chemical composition.* The mineral is to be classed under the general division *Hydrous Sulphates.*

A. Elements in the protoxide state.

(*e*) Epsomite group, containing iron, zinc and manganese.

The mineral under consideration very closely resembles Fauserite, which is a sulphate of manganese and magnesium, containing 40 per cent. of water of crystallization whose formula is

$$MgO.SO_3+2MnOSO_3+15HO.$$

The analyses of the manganese mineral under consideration lead to the formula

$$FeO.SO_3.ZnO.SO_3.5MnO.SO_3+28HO,$$

or, adopting the atomic weights now in use,

$$FeSO_4.ZnSO_4.5MnSO_4+28H_2O.$$

The results of a number of analyses are here given:

Residue, chiefly SiO_2.	ZnO.	FeO.	MnO.	HO.	SO_3.
0.54 per ct.	5.63 per ct.	4.12 per ct.	22.92 per ct.	29.88 per ct.	35.88 per ct.
0.75 "	6.23 "	3.73 "	21.78 "	32.54 "	35.84 "
0.60 "	..	4.18 "	21.92 "	29.94 "	35.93 "
..	..	4.55 "	22.06 "	31.44 "	36.20 "
..	..	..	..	32.14 "	36.11 "
..	..	.	..	32.78 "	35.77 "
..	..	.	..	31.82 "	35.85 "
..	..	..	..	30.58 "	..

Taking the average of all these results and correcting for the residue we have the figures given below. With them are also given the percentages required by the formula already stated:

	Average results. corrected for residue.		Calc. for formula $ZnO.SO_3.FeO.SO_3.5MnO.SO_3+28HO$.
FeO	4.18 per ct.	. .	4.58 per ct.
ZnO	5.97 "	. .	5.15 "
MnO	22.31 "	. .	22.58 "
SO_3	36.07 "	. .	35.62 "
HO	31.60 "	. .	32.06 "

The mineral has a bitter, astringent taste. It is very readily soluble even in cold water. The aqueous solution effervesces with sodium carbonate, and reddens blue litmus paper. Ammonium sulphocyanide does not give a test for sesquioxide of iron. Upon boiling the water solution, a very slight iron precipitate is formed.

Masses of the mineral, together with the gangue, were treated with pure distilled cold water, and, after digesting some minutes, the solution was filtered through double filter paper. The residue was then treated in a stream of water for a long time, thereby eliminating the lighter portions. The matrix was then dried and subjected to blow-pipe tests, which showed the presence of the sulphides of iron, lead and zinc. There were also detected manganese and some willemite. The gangue is a quartzose rock containing the above-named sulphides. On exposing the moist gangue, entirely freed from the soluble mineral, to the action of moisture and air, the mineral sulphides were found to become oxidized readily, giving strong reactions for sulphuric acid.

The filtrate was cautiously evaporated, a stream of hydrogen gas being passed through the liquid to prevent the oxidation of the

iron. Only by evaporating quite low were any crystals obtained, and then they were small unless great care was taken. I have succeeded in obtaining large, handsome crystals.

4. *Locality.* The mineral is found in Hall Valley, Park County, Colorado, upon the McDonnell mining property. This "claim" is near Middle Swan Creek, and 13 miles from Webster, situated on the Denver and Rio Grande R. R. The vein is located above timber line, the apex of location being in frozen snow. The gangue is over 300 feet wide, and shows upon the rocks this efflorescent salt. There is said to be a trace of gold and silver contained in the gangue for the above-mentioned entire distance. The gangue after being freed from the soluble mineral gave by fire assay at the office of the Grant Smelting Co. 9 ozs. silver per ton (2000 lbs.). In some places there is a pure streak of this mineral of 2 to 8 inches in width.

The McDonnell property has been developed by a tunnel 40 feet long, and has a shaft upon the claim 35 feet deep. During the excavations this mineral is brought to light. I am indebted to Mr. Frank Maloney for a description of the locality, etc.; also to Mr. Wm. R. Boggs, who gave me excellent samples for analysis. In conclusion, I will state that any parties may obtain samples for further scientific investigation by application to the writer. I have sent some of the best samples to Prof. Ira Remsen for more exact study and statements than I have made.

GRANT SMELTING CO., LEADVILLE, COLORADO.

ON THE SEPARATION AND DETERMINATION OF POTASH AND SODA BY THE INDIRECT METHOD IN PLANT ASHES, FERTILIZERS, AND SIMILAR SUBSTANCES.

BY CLIFFORD RICHARDSON.

Collier has shown[1] that with mixtures of pure chlorides of potassium and sodium, the indirect method is capable of furnishing very accurate results; but, in attempting to apply it to the determination

[1]Amer. Journal of Sci. 1864, 346.

of potash and soda in the ashes of plants, I have found that the usual manner of separating the mixed chlorides of the alkalies for subsequent determination of chlorine and calculation of the relative amounts of potassium and sodium, does not furnish them in a state of sufficient purity for the accuracy which this process requires.

Instead of the usual method of procedure, the following has been found to give the chlorides in perfectly pure condition. The impurities which are usually met with and resist removal are phosphoric acid and magnesia, and the latter can only be completely and easily displaced in the absence of all strong acids. For this reason the ash is dissolved in nitric acid and evaporated several times, to be sure of the conversion of chlorides to nitrates. It is then taken up with water and a few grams of oxalic acid added, and again evaporated once or twice on the steam-bath. The nitrates are in this way converted to oxalates, and, on gentle ignition, to carbonates. There then remain only phosphates, sulphates and carbonates. The residue is to be taken up with water and filtered through a filter as small as possible, removing as phosphate and sulphate of lime and as carbonate of lime and magnesia the greater part of these acids and bases. To the filtrate a slight excess of barium hydrate is added, and, after boiling and subsequent filtration, there remain in solution nothing but the alkalies as hydrates and the excess of barium. To insure complete freedom from magnesia, however, the filtrate is evaporated to dryness, much of the barium, as well as the alkalies, being at the same time converted to carbonates. The residue is treated with successive portions of water, not more than 5 cc. at a time, and filtered through a filter 7 cm. in diameter. To the filtrate, carbonate of ammonia, as free from empyreumatic matter as possible, is added, and after evaporation to dryness, to remove the excess, the residue is taken up with water again, and filtered through a small filter into a weighed platinum dish. This is to be covered with a watch-glass and the purest hydrochloric acid added, to convert the carbonates of the alkalies to chlorides. After evaporation and gentle ignition, a slight black carbonaceous residue will be found, which must be removed by filtration. The solution is then again evaporated, heated to 130° and weighed. The chlorides are quite pure, being clear white, and ready for the determination of chlorine.

This process has been in use for the past three years in the laboratory of the Department of Agriculture, and has given most satisfactory results.

The usual method with platinum has a tendency to throw all the error into an exaggeration of the amount of sodium present, especially if the mixed chlorides are impure; and in this way many of the older analyses show a percentage of sodium in the ashes of plants which most of my analyses, as carried out by this more careful method, do not confirm. For example, in the ashes of thirty-four grasses analyzed in 1878 sodium was found in only eighteen, and then in only two cases in amounts exceeding two per cent.; and in ten analyses of cereals sodium was found in none.

In fertilizer and soil analyses this method finds, also, a very convenient application.

WASHINGTON, D. C., *Oct.* 1881.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XI.—ON THE CONDUCT OF NITRO-META-XYLENE TOWARDS OXIDIZING AGENTS.

BY IRA REMSEN AND M. KUHARA.

The experiments described in this paper were undertaken for the purpose of determining whether a nitro-group situated in the ortho-position with reference to an oxidizable residue in a benzene compound exerts a protective influence when the compound is subjected to the action of certain oxidizing agents. The influence of the sulphonic acid group and of its derivative, the sulphamide group (SO_2NH_2), has been determined in several cases, and the results have been recorded in earlier papers of this series. The question suggests itself, Does the nitro-group act like the sulpho-group? The facts thus far determined are not sufficient to warrant a satisfactory conclusion, though they make an affirmative answer appear probable, at least for such compounds as contain two oxidizable residues together with the nitro-group.

The particular case considered in this paper is that of the nitro-compound formed by treating metaxylene with nitric acid. It

was shown by Beilstein and Kreusler[1] that, when the nitro-compound or compounds obtained by treating ordinary xylene with nitric acid, are oxidized, only one of the methyl groups contained in the compound is changed to carboxyl, the product being a nitrotoluic acid. Commenting upon this fact, the authors say: "Offenbar bewirkt Eintritt negativer Elemente oder Radicale in den Kohlenwasserstoff dass derselbe widerstandsfähiger gegen Oxidationsmittel wird. Aehnliche Erscheinungen finden sich häufig." The orientation of the groups in the compound was not determined at the time. Later experiments proved that the compound is a derivative of metaxylene. Beilstein himself showed[2] that when the amido-metatoluic acid corresponding to the nitrotoluic acid above referred to is distilled with lime it yields ortho-toluidine. From these facts we may conclude that in the nitrotoluic acid the nitro-group and methyl-group are in the ortho-position relatively to each other, and that the carboxyl is in the meta-position relatively to the methyl. Whether the nitro-group is in the ortho- or the para- position relatively to the carboxyl cannot be decided without the aid of further experiments. It is known that when bromine acts upon metaxylene the orientation of the three groups in the product is expressed by the formula $C_6H_3.Br.CH_3.CH_3$ (1.2.4), and Wroblewsky[3] concluded that in nitrometaxylene the groups probably stand in the same relation to each other. Hence he gave to the compound the formula $C_6H_3.NO_2.CH_3.CH_3$ (1.2.4). This would lead to the formula $C_6H_3.NO_2.CH_3.CO_2H$ (1.2.4) for nitrometatoluic acid. Assuming this to be correct, the further conclusion is justified that, when nitrometaxylene is oxidized with chromic acid, the nitro-group protects the ortho-methyl group, while the para-methyl is converted into carboxyl. But the proof for the formula of nitrometaxylene can hardly be regarded as conclusive; and, further, as Beilstein's investigation was undertaken before it was known that ordinary commercial xylene is a mixture, it appeared possible that the nitrotoluic acid described by him might also be a mixture. It is hence plain that in order to reach positive conclusions the transformations above alluded to must be reinvestigated, and new experiments must determine the nature of the nitrotoluic acid from nitrometaxylene.

1 Annalen der Chemie, **144**, 168.
2 Zeitschrift f. Chemie, 1869, 524.
3 Berichte der deutschen chemischen Gesellschaft, **9**, 497.

Preparation of Nitrometatoluic Acid.[1]

A large quantity of commercial xylene (from Kahlbaum's factory) which was found to consist mainly of the meta-variety, was boiled for a long time with dilute nitric acid, for the purpose of destroying, as far as possible, the para-xylene. The hydrocarbon left unacted upon was then distilled off with water-vapor, washed with ammonia, dried and rectified. It was found to be necessary to continue the boiling with nitric acid for from thirty to forty hours. The purified metaxylene was converted into the mononitro product, according to the method described by Beilstein and Kreusler.[2] Instead of distilling with water from a copper retort, we found it more convenient to distill from a large glass flask into which a constant current of steam was passed. The process can be carried on in this way without difficulty.

For the oxidation of the nitroxylene Beilstein and Kreusler[3] recommend the use of this mixture: 20 grams nitroxylene, 40 grams potassium pyrochromate, and 55 grams concentrated sulphuric acid diluted with twice its volume of water. As a considerable quantity of the nitroxylene escapes the action of the chromic acid when the above proportions are used, some experiments were made to determine whether the quantity could not be advantageously reduced. Further, as the time suggested for the oxidation is only six to eight hours, it was thought that by heating longer the yield might possibly be increased. It is unnecessary to describe our experiments in detail, as they all gave negative results, and only served to show that the first recommendations are really the best. Accordingly, in the preparation of nitrotoluic acid we have since followed closely the original directions. The yield is by no means satisfactory.

In order to determine whether, when nitroxylene is oxidized, the product is a single substance or a mixture, the acid precipitated from its solution in sodium carbonate was carefully washed and then converted into the calcium salt. The mother-liquor containing sodium carbonate was further evaporated, and all the acid which could be obtained from this was collected and examined. The calcium salt was easily obtained in crystallized form, and consisted

[1] The first experiments described in this paper were performed with great skill by Mr. Hermann Voorhees, one of the most promising young men I have ever had the good fortune to be associated with. His work was suddenly interrupted by a serious attack of illness, from which he soon afterward died. May these few words serve as a token of the respect and admiration felt for him by those who knew him here.—I. R.

[2] Annalen der Chemie, **144**, 167.

[3] *Loc. cit*

then of thin prisms radiating from a centre. By far the largest quantity of the salt was obtained in this form, while from the last mother-liquors there was deposited a less pure substance consisting of crystalline crusts. It was at first thought that this substance was a second salt. On being repeatedly recrystallized, however, it gradually assumed the form of the pure calcium salt first deposited. A very small quantity of material was obtained from the very last mother-liquors, which could not be purified by crystallization. Its quantity was too small to permit of a careful examination. The acid precipitated from it had nearly the same fusing-point as that precipitated from the pure salt; the fusing-point was, however, not constant. As, in the course of our examination we worked up about forty or fifty grams of nitrotoluic acid and obtained from this only a very minute quantity of an impure calcium salt from the last mother-liquors, the conclusion is justified that when nitroxylene is oxidized with chromic acid only one nitrotoluic acid is formed. Whether this is due to the fact that the nitroxylene itself is a single substance, or to the fact that only one constituent of the original mixture is capable of yielding an acid by oxidation, must for the present remain an open question.

The calcium salt above-mentioned was analyzed and gave these results:

I. 0.2023 gram salt lost 0.0169 gram H_2O at 150°; and gave 0.0627 gram $CaSO_4$.

II. 0.2713 gram salt lost 0.0211 gram H_2O at 185°; and gave 0.0848 gram $CaSO_4$.

	Calculated for formula $\left(C_6H_3\left\{\begin{matrix}NO_2\\CH_3\\CO_2\end{matrix}\right.\right)_2Ca+2H_2O.$	Found. I.	II.
Ca	9.17	9.12	9.19
H_2O	8.26	8.35	7.78

After the water of crystallization is driven off by heating to a high temperature, if the salt is allowed to stand in contact with the air it rapidly takes up one molecule of water. Even by standing in the balance-case, in which there was a good-sized vessel containing sulphuric acid, the salt absorbed one molecule of water in the course of a few hours. In two different specimens, which had been heated up to 180° and from which all the water was driven off, there were found respectively 4.68 per cent. and 4.68 per cent. water

after standing. The formula, $(C_6H_3NO_2.CH_3.CO_2)_2Ca+H_2O$, requires 4.31 per cent. H_2O.

The nitrotoluic acid precipitated from the calcium salt fused at 211° (uncorr.). On recrystallizing it from water, however, and then purifying it further by sublimation, the fusing-point was found to be 214° (uncorr.). The fusing-point of the acid precipitated from the calcium salt was not changed by repeated crystallizations of the salt.

Transformation of Amido-toluic Acid into Oxytoluic Acid.

Pure nitrotoluic acid was converted into amido-acid by treating it with strong hydrochloric acid and tin according to the directions of Beilstein and Kreusler. The amido-acid was easily obtained in pure condition, and was found to have the properties ascribed to it by its discoverers. They transformed a small quantity of the acid by means of Griess's reactions into the corresponding oxy-acid, but were unable to obtain the latter pure. In regard to it they say: "Wir erhielten die p-Oxytoluylsäure in Gestalt kleiner gelblicher Prismen. Die Säure ist in kaltem Wasser schwer, in heissem leicht löslich. Sie scheint ein Molecul Krystallwasser zu enthalten. . . . Die kleine Menge der erhaltenen Substanz erlaubte keine eingehenden Reinigungsversuche."

To obtain this oxy-acid in larger quantity and pure condition, a few grams of the amido-acid were dissolved in the smallest possible quantity of dilute nitric acid. A slow current of nitrous acid (from nitric acid and arsenic trioxide) was conducted into the well-cooled solution, when the diazo-compound was precipitated in the form of white crystals. After allowing the solution to stand for a short time until all the diazo-compound appeared to be deposited, the latter was rapidly filtered off through asbestus with the aid of an aspirator, and quickly dried by bringing it on unglazed porcelain. The pure dry substance was now brought into a large quantity of water and the solution boiled. A strong evolution of gas took place. When this ceased the solution was neutralized with ammonia. This caused the liquid to turn a dark brown color. It was evaporated to a small volume and acidified, when the oxy-acid was precipitated as a brown powder. It was dissolved in water and boiled with bone-black, by which all the color was removed, and, on concentrating the solution, the acid crystallized out.

The acid thus obtained crystallizes in fine, lustrous, silky needles. It is difficultly soluble in cold water, but easily in hot water. The solution is not colored by ferric chloride. It is easily soluble in cold alcohol and ether, but insoluble in bisulphide of carbon. It melts at 148.5°–149.5° (corrected). After drying at 100° it melts at 174° (corrected). It was analyzed with the following results:

I. 0.1682 gram air-dried acid lost 0.0097 gram H_2O at 130°.

			Calculated.	Found.
$C_8H_8O_3$	...	152	94.41	...
$\frac{1}{2}H_2O$	...	9	5.59	5.77

II. 0.1534 gram acid dried at 130° gave 0.3546 gram CO_2 and 0.0825 gram H_2O.

		Calculated.		Found.
C_8	...	96	63.16	63.03
H_8	...	8	5.26	5.97
O_3	...	48	31.58	...
		152	100.00	

The results agree, as will be seen, with those required by oxytoluic acid of the formula $C_6H_3\begin{cases}OH\\CH_3\\CO_2H\end{cases}+\frac{1}{2}H_2O$. The formula and all the properties of the acid indicate clearly that it is identical with the oxytoluic acid of Remsen and Iles,[1] obtained by them from sulphamine-metatoluic acid by fusing this with potassium hydroxide. The structure of the acid was shown to be $C_6H_3\begin{cases}OH(1)\\CH_3(2)\\CO_2H(4)\end{cases}$. The same acid was prepared by Tiemann and Schotten[2] by an entirely different method, which consisted in introducing the aldehyde group into ortho-cresole and oxidizing the aldehyde thus obtained. They called it ortho-homo-paroxybenzoic acid. The experiments of Tiemann and Schotten also lead to the conclusion that the structure of the acid is correctly represented by the above formula.

The experiments thus far described suffice to show positively that the structure of the nitrotoluic under investigation is that which was anticipated. As by simple, clean reactions we have

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 888; and this Journal, **1**, 48, 114.
[2] Berichte der deutschen chemischen Gesellschaft, **11**, 767.

passed from the nitro-acid to an oxy-acid of the formula $C_6H_3 \begin{cases} OH(1) \\ CH_3(2) \\ CO_2H(4) \end{cases}$ it follows that the orientation of the groups in the nitro-acid must be represented by the formula $C_6H_3 \begin{cases} NO_2(1) \\ CH_3(2) \\ CO_2H(4) \end{cases}$ The conclusion is hence justified that the nitro-group in nitroxylene, being situated in the ortho-position relatively to one methyl-group and in the para-position to the other, protects the former from oxidation when the compound is treated with the chromic acid oxidizing mixture. This fact serves as a new illustration of the protective influence exerted by negative groups, to which attention was first called in this series of papers. It will be seen, further, that between the sulphonic acids of xylene and the nitro-product there is a close resemblance. When xylene is treated with sulphuric acid, the main product is a sulphonic acid of the same structure as the nitroxylene above considered. By oxidation and subsequent fusion with potassium hydroxide it is converted into the same oxy-acid as that obtained from nitro-xylene. There is, however, a second sulphonic acid formed, in which the sulpho-group is in the ortho-position relatively to both methyl-groups. By oxidation with chromic acid this disappears, and a single product corresponding to the principal sulphonic acid is obtained. Now, it may be that the original nitro-xylene is a mixture of two substances, analogous to the two sulphonic acids, and that only one of these yields an oxidation product, the other being destroyed.

The transformations above considered may be conveniently represented thus:

$C_6H_3 \begin{cases} NO_2 \\ CH_3 \\ CH_3 \end{cases}$	$C_6H_3 \begin{cases} NO_2 \\ CH_3 \\ CO_2H \end{cases}$	$C_6H_3 \begin{cases} NH_2 \\ CH_3 \\ CO_2H \end{cases}$	$C_6H_3 \begin{cases} OH \\ CH_3 \\ CO_2H \end{cases}$
Nitro-xylene.	Nitrotoluic Acid.	Amidotoluic Acid.	Ortho-homo-paroxybenzoic Acid.

Transformation of Amidotoluic Acid into Chlor- and Brom-metatoluic Acids.

Chlortoluic Acid.—Some of the diazo-compound obtained from amidotoluic acid was boiled with concentrated hydrochloric acid. While boiling, a crystallized substance separated. It was purified

by boiling with bone-black and then crystallized from alcohol. It is almost insoluble in cold water, and but slightly in boiling. It is slightly soluble in cold alcohol, but quite easily in hot. It crystallizes from alcoholic solution in groups of nearly colorless fine needles. From a mixture of alcohol and water it is deposited in lustrous needles. It fuses at 204° (corrected), and sublimes easily. An estimation of chlorine was made by heating with lime.

0.1448 gram acid gave 0.1222 gram AgCl.

		Calculated for $C_8H_7ClO_2$.	Found.
Cl	...	20.82	20.85

The substance is a chlortoluic acid of the structure $C_6H_3\begin{cases} Cl(1) \\ CH_3(2) \\ CO_2H(4) \end{cases}$. It is identical with the so-called para-chlortoluic acid of Vollrath[1] obtained by the oxidation of chlorxylene with chromic acid. The above transformation furnishes the proof that when chlorxylene is oxidized, the chlorine atom which occupies the ortho-position relatively to one of the methyl-groups protects the latter from oxidation. The phenomena studied in connection with the nitro-product are repeated in connection with the chlorine-product.

Bromtoluic Acid.—This acid was prepared like that just described. While boiling, the product separated in the form of a crystalline powder. It was recrystallized from alcohol and obtained perfectly white. It is almost insoluble in cold and hot water. It is slightly soluble in cold alcohol, but quite easily in hot. It fuses at 205°–206° (uncorr.) or 208°–209° (corrected). A bromine determination was made with the following results:

0.25 gram air-dried acid gave 0.22317 gram AgBr.

		Calculated for $C_8H_7BrO_2$.	Found.
Br	...	37.2	37.98

The acid is $C_6H_3\begin{cases} Br(1) \\ CH_3(2) \\ CO_2H(4) \end{cases}$. Its properties are the same as those of the bromtoluic acid obtained by Fittig, Ahrens and Mattheides[2] by oxidizing bromxylene. There can be little doubt that the two are identical. Hence it is seen that when bromxylene is oxidized, the ortho-methyl-group is protected.

[1] Annalen der Chemie, **144**, 266.

[2] Annalen der Chemie, **147**, 32.

Although the above experiments prove conclusively that the substances examined are derivatives of metaxylene, it seemed desirable to transform the amido-acid into metatoluic acid. For this purpose the usual method of boiling with alcohol was employed. But instead of obtaining metatoluic acid, a well-crystallized acid, fusing, when purified, at 198°, was the result. This acid is insoluble in cold water, and only slightly in hot water. It crystallizes from an alcoholic solution. It is volatile with steam. It sublimes in light flakes. The analysis did not give satisfactory results. With the small quantity at our disposal it was impossible to determine what the acid is. Mr. P. H. Broun is at present engaged in preparing a larger quantity of it for the purpose of careful study, and in a short time the result of his examination will be made known.

Xylidine.—As we had in our possession a considerable quantity of nitroxylene, which was recovered from the oxidizing mixtures, it was thought best to examine this carefully for two purposes: (1) To determine whether this unoxidized material is the same nitroxylene as that which yields the nitrotoluic acid; and (2) whether it is a single substance or a mixture.

For the first purpose some of the product was treated again with the chromic acid mixture. The same nitrotoluic acid was obtained as in the first operation, and the quantity of the product was about the same. The nitroxylene recovered from this operation was again oxidized, and again yielded the same nitrotoluic acid. Hence it follows that this nitroxylene at least contains a considerable quantity of the substance which in the first oxidation yielded the nitrotoluic acid.

To determine whether the substance is a mixture or not it was transformed by means of tin and hydrochloric acid into the corresponding xylidine. After drying the xylidine it was treated with acetyl chloride and thus converted into the acetyl compound. By crystallizing from alcohol and water this was readily obtained in pure condition as very fine, lustrous needles. It dissolves readily in alcohol; is difficultly soluble in cold water, and not very easily in hot water. It fuses at 127°-128°. The properties are the same as those of the α-xylidine of Hofmann, the xylidine of Wroblewsky from metaxylene, and the α-xylidine obtained by Schmitz from α-amidomesitylenic acid. The experiments of Wroblewsky[1] and

[1] Berichte der deutschen chemischen Gesellschaft, 9, 497.

of Schmitz[1] have shown that the formula of this compound is $C_6H_3\left\{\begin{array}{l}NH_2(1)\\CH_3(2)\\CH_3(4)\end{array}\right.$, and our experiments confirm the formula. The nitroxylene used by us certainly consisted almost entirely of the one modification. The α-xylidine obtained from it was, as has been said, nearly pure. Some foreign substance contaminated it slightly; but, whatever the impurity may have been, its quantity was so small that it was impossible to separate it, and it was not sufficient to render inaccurate the statement that the nitroxylene recovered from the oxidizing mixtures is essentially a pure compound.

JANUARY, 1882.

REVIEWS AND REPORTS.

TRAITÉ DE CHIMIE GÉNÉRALE, COMPRENANT LES PRINCIPALES APPLICATIONS DE LA CHIMIE AUX SCIENCES BIOLOGIQUES ET AUX ARTS INDUSTRIELS: par PAUL SCHÜTZENBERGER, Professeur au Collège de France. 2 Vols. Paris. 1880.

Although more than a year has passed since this book appeared, no apology is necessary for calling special attention to it, even at this late day. Among the many text-books of chemistry that have been given to the public during the past few years, this one stands out prominently. It must be classed among the very best. The one characterizing feature of the book is objective treatment. The facts of chemistry are brought prominently forward, and the strictly logical conclusions which these facts warrant are then considered. There is an entire lack of the wild theorizing which plays such an important part in many inferior text-books of the last decade, and which has done so much to bring chemistry into disrepute. Many of these text-books are quite unintelligible to a chemist, not to say to the young student for whom they are intended. What conception can a writer have of the science of chemistry and the mental powers of students when at the outset of his presentation he discusses "types," "molecules," "equivalence," "atoms," "hydroxyl-groups," "structure," etc., etc.? Yet we need only pick up at random one of the recent books: the chances are that we shall

[1] Annalen der Chemie, 193, 177.

find these subjects taken up in the first twenty or thirty pages. If this is not so, then at least we shall find in some part of the book a chapter or two devoted to "theoretical chemistry," made up largely of dogmatic statements, which are sprung upon the reader without warning. Thus: "Nitryl (NO_2) is a negative compound radical"; "In sulphuric acid sulphur is a hexad, and there are two hydroxyl groups present in the acid"; "When to each of the bonds of a multivalent radical is united an atom of the same kind . . . the forces exerted at the several points appear to be . . . equal"; "The nitrogen atom has usually three bonds, although sometimes it has five"; etc. While these statements may be justified in some instances, if the facts upon which they are based are known, it certainly can do no good to make them without showing exactly how the facts lead to them.

From the kind of errors just referred to, the book in question is singularly free. In the introduction indeed the author clearly states his intention of keeping theory subject to facts. As, after a careful examination of the book, it seems to me that the author has admirably succeeded in doing what he intended to, I can not perhaps do better than to quote freely from his introduction.

In speaking of the changes in the views of chemists concerning the true nature of chemical phenomena, the author says: "The study of these changes teaches us how necessary it is to be distrustful and skeptical when we leave the domain of facts and enter that of hypothesis." . . . "Far be it from us to condemn the powerful efforts of thinkers who seek to utilize the vast material put at their disposal by their predecessors and increased by their own discoveries." . . . "Theory is not only useful, but even indispensable to the chemist; it is the beacon which guides him towards the unknown." . . . "But it is necessary to recognize and avow that the beacon is still dim and can only serve for short distances." On page iv. we read: "Without going farther, let us say at once . . . that between what is at present called the *atomic theory* . . . and the very old *hypothesis* of atoms and of discontinuous matter, there is only a very weak bond." The notion of atoms and of discontinuous matter is an hypothesis and nothing more.

"The atomic theory has its origin, on the contrary, in experiments. It is founded on facts fixed and undeniable, from which it is deduced by legitimate processes. It is *independent* of the hypothesis of atoms, and is connected with it only through a figurative language, and a nomenclature of which it would perhaps be well to rid itself.

"The chemical atom does not *necessarily* constitute a small indivisible mass, invariable in weight, form and volume. The chemical atom is for us only *the smallest ponderable quantity of an element which can take part in a reaction*. We regard this *smallest quantity* not as an absolute value, but as a relation; and if we fix it by a number, it is solely for the sake of comparison with the base of the system of notation adopted.

"Newton, in explaining the system of the moon by universal attraction, took care to add that things act *as if* masses mutually attract each other at a distance. In chemistry we can also say . . . : Things conduct themselves *as if* atoms or particles attract each other and unite to form complex molecules. But it is impossible for us to go farther and to admit that a particle of chlorine, for example, *really* possesses a special attractive force. . . These occult and special forces, which we are obliged to attribute to the atoms to explain each order of facts, are very little in harmony with the grand thought of the unity of the forces of nature. . . This unity should extend to chemical phenomena as well as to physical phenomena. The conquests of thermo-chemistry furnish proof positive that intimate relations exist between a chemical reaction and the manifestations of heat, of electricity and of light. . . The unity of the forces of nature is not merely a vague aspiration of the mind: it appears to us as a truth, and as one of the greatest conquests of science, founded as it is on transformation of the forces, demonstrated by experiments, both qualitative and quantitative. It gives great weight to the idea of the unity of matter of which it is the sister."

These quotations will serve to illustrate the spirit of the author as exhibited throughout the book.

The subject is taken up under three general heads: (1) GENERAL PHENOMENA; (2) ELEMENTS OR SIMPLE BODIES; (3) SPECIAL STUDY OF THE ELEMENTS. The first subdivision occupies something over a third of the first large volume, and is to the advanced student the most interesting part. The subjects of the seven chapters which make up this part of the book are: (I) *Object and aim of Chemistry—Definition of the general phenomena with which it has to deal;* (II) *Nomenclature and Symbols;* (III) *Physical character of bodies;* (IV) *Of Affinity and chemical phenomena in general;* (V) *Numerical laws and relations by weight according to which chemical combinations take place;* (VI) *Determination of Equivalents;* (VII) *Principles of Thermo-chemistry.*

It would lead too far to attempt to give an adequate idea of the author's method of treatment of the subject-matter under each of the heads above named. In general, it may be said that the subjects are treated more fully than is usual in text-books of chemistry, and the relations of the subjects to chemistry as a science are kept more clearly in view than is usual. Thus we find in chapter III. admirable treatment of the subjects of: The nature of gases; the diffusion of liquids or molecular diffusion; osmose; dialysis; and gaseous diffusion. The principal investigations to which we owe our present knowledge of these subjects are clearly described, so that the connection between what has been done in the way of experiments and the conclusions which are drawn is easily recognized; and the reader unconsciously becomes familiar with the methods of experiment which have been employed in each case. For an earnest

student of chemistry, who really desires to master the subject, I cannot think of a better exercise outside the laboratory than a careful reading of this book. The original papers, the results of which are discussed, should also be read; and as references to them are given in the proper places, the finding of these papers is facilitated.

The chapter on Affinity is of special interest. It opens with an historical review, in which the views of the earliest investigators are first given, and the changes in the prevailing views are clearly explained. The laws of Berthollet receive due attention. Speaking of the final overthrow of the electro-chemical theory of Berzelius, the author says: "In fact, the time has not yet arrived when we can seek to form an approximate idea of the cause of combination. This cause must be studied in its various manifestations before we become attached in too absolute a way to premature hypotheses. Without doubt, the mechanical theory of heat is destined to throw great light on the manifestations of chemical action; and, in the near future, we shall see chemistry become connected with the physical sciences by indissoluble bonds. I recall here the profound words pronounced at the Chemical Society of Paris by my illustrious master, M. Sainte-Claire Deville: 'Affinity, considered as a force, is an occult cause; if it is only the expression of a quality of matter, it ought to serve solely to designate the fact that such and such substances can combine under such and such well defined circumstances. All the investigations, all the tendencies of modern science, lead to the identification of the forces which act in the physical and chemical phenomena of nature. All numerical determinations tend to establish their equivalence. . . Affinity and cohesion cannot escape this identification, and already the mechanical theory unites them in a circle of arguments which ought soon to cause the disappearance of whatever they present that is vague and mysterious.'"

More than twenty pages are devoted to the interesting and important phenomena of dissociation. This is considered necessary because "dissociation has led chemists to modify to some extent their ideas concerning chemical action." The experiments of Sainte-Claire Deville are fully described, and everything that is of importance for an understanding of the phenomena is discussed.

The problem of determining atomic weights and equivalents is fully considered in chapter VI. The determination of equivalents is, in the first place, of course purely experimental, involving difficulties, to be sure, but not involving hypothesis. The object is to find "by analytical or synthetical methods, that is to say by means of the balance, the weights of the various elements which unite with a given weight of one of them taken as a term of comparison." There is, however, another thing to be done; that is, "to select, among the possible multiples which might be adopted, that one which agrees best with the analogies in the properties or with the accepted theoretical ideas." For the purpose of making this

selection, or, as we commonly say, for the purpose of determining the atomic weights, the author acknowledges the value of considerations based on the study of the phenomena of isomorphism, of specific gravity of vapors and of specific heat, and shows himself thus to be in harmony with the majority of chemists of the present day. His remarks on this subject in general are worthy of special notice. He is certainly not carried away by theories, nor does he go to the other extreme, as did St. Claire-Deville, and as Berthelot does now. Our author, a pupil of St. Claire-Deville, is evidently more inclined than his former teacher to acknowledge the value of some of the prominent views prevalent among chemists. And he justifies himself thus:

"We have thus far shown that simple relations exist between the numbers expressing the proportions by weight according to which bodies unite, react upon each other, are replaced one by another, and (1) the crystalline form, (2) the density in the form of gas, (3) the specific heat.

"Systems of equivalents or atomic weights might be established, satisfying either the conditions of isomorphism or those of the hypothesis of Avogadro, or again the law of Dulong and Petit. In the first case, the atomic weights would give similar formulas to all isomorphous bodies; in the second, all compounds would have equivalents or molecular weights corresponding to the same volume; finally, in the third place, the product of the specific heat of an element by its atomic weight would be equal to a constant. If the three systems thus established agree in the great majority of cases; if, further, the single system resulting from the three orders of phenomena does not meet with any serious contradiction in the facts of chemistry, there would be reason to adopt it with confidence, for it will be in entire harmony with the programme laid down above, with the greatest number of analogies. It is, in fact, this conclusion which we reach on taking all the known facts into consideration."

Again, p. 252, he says: "Attaching to the equivalent weights no hypothetical idea regarding the intimate constitution of matter, and taking no other guide in the choice of the numbers selected than the need of recalling and symbolizing the largest possible number of analogies, we are led to use the system most commonly employed at the present day in chemical text-books and memoirs—that which is known under the name of the *system of atomic weights*. It appears according to its designation to be based on the hypothesis of atoms. In reality it finds its strongest support in the facts and sums up in a satisfactory manner the principal results of experiment.

"As regards the atomic hypothesis itself, it should be considered merely as an image, a figurative comparison, intended to render more comprehensible and to emphasize the relations of the facts among themselves, to materialize, so to speak, the results of experiment; moreover, it is conducive to clear and precise language.

"The words atoms, molecules, mono- or polyvalent atoms, and all others of the prevalent nomenclature, correspond undeniably to experimental realities, and are deduced from important considerations, the fruit of long and brilliant investigations; but an unrestricted and absolute sense should not be attached to them."

This caution is undoubtedly in the interest of truth, for it is certainly of the highest importance that chemists should be able to recognize exactly where their knowledge of facts ceases and where the products of speculation begin to appear. No matter how perfectly the hypothesis may be in accordance with the facts, we must not forget that it is hypothesis.

Chapter VII. is devoted to the principles of thermo-chemistry. Here again we have the same clear and satisfactory treatment. In the space of fifteen pages the phenomena of thermo-chemistry, the methods of investigation, and the results achieved by Thomsen and Berthelot, are very satisfactorily explained. Referring to the fundamental principle of thermo-chemistry, that "the heat evolved or absorbed during a chemical transformation . . is the tangible representative of the molecular work accomplished during the change of state, and is equivalent to the loss or gain of energy experienced by a system of bodies reacting upon each other," the author says, page 256: "The preceding principle is nothing but that of equivalence of heat and work applied to molecular mechanics.

"M. Thomsen expressed similar ideas in 1853, although in terms less in harmony with the theories now in vogue. In *Die Grundzüge eines thermochemischen Systems*, he says: 'The total heat developed in a reaction is a measure of the loss of chemical force resulting from the act of combination. For the same body and the same temperature, the intensity of chemical force is constant.' Replacing the words *intensity of chemical force* by *energy*, we substitute a precise meaning for a vague and badly defined idea. This criticism, however, takes away nothing essential from the important conclusions drawn by Thomsen from his statement.

"M. Deville had very nearly the same idea concerning affinity as that expressed by Thomsen. He used the expression *latent heat* instead of energy. Lavoisier and Laplace admitted that the decomposition of a body into its elements absorbs as much heat as the combination of the elements had produced. . . The calorimetric experiments of Andrews, of Hess, of Th. Woods, of Favre and Silbermann, and the more recent ones of M. Berthelot and M. Thomsen, all tend to verify this direct consequence of the application of the mechanical theory to chemistry."

While in the parts of the book already referred to the best opportunity is given for originality of treatment, the remaining portions will by no means be found to be conventional. In nearly every chapter something will be found which is worthy of special study, and which is not commonly met with even in advanced textbooks.

In the chapter on the Physical Properties of the Elements the most important contributions to spectroscopy are considered. M. Salet's methods of observing the spectra of vapors and gases; Masson's apparatus for observing the spectra of metals; Lecoq de Boisbaudran's burner for spectroscopic work; the same chemist's apparatus for observing the spectra of sparks; the tube of Delachanel and Mermet for spectroscopic observations, are all carefully described, and the descriptions are rendered clear by excellent woodcuts.

Passing on to Book Third, which has to deal with the special study of the elements, the interest is kept up, for we find a great many facts emphasized which are usually not mentioned at all, or, if mentioned, only in such a way as to lead the student to think that they are of very little importance. Special care is taken in devising experiments to illustrate the important physical properties of substances. A number of the experiments described are original, and others are new to chemical text-books.

While fully impressed with the paramount importance of the purely scientific side of his subject, the author does not lose sight of, or undervalue, the practical questions which present themselves. The methods used for manufacturing chlorine and oxygen on the large scale; for extracting sulphur from its ores; a new apparatus for the refining of sulphur; the apparatus for refining phosphorus; an apparatus for the manufacture of bone-black, and many other methods and forms of apparatus are very fully described and illustrated.

But I have perhaps said enough to awaken interest in the book among those who may read this notice. That is all I desire. I believe that the tendency of the book is excellent, and, though undoubtedly many things might be pointed out in regard to which there may be two opinions, and other matters might be censured, I am sure that the book is freer from errors of judgment and of execution than is usually the case. I believe that the author's method of presenting the subject is the right one, and that if most of our teachers could become imbued with his spirit, we should have less crudeness of thought among our young men—and old, for that matter. In learning chemistry we want first a solid foundation of facts, such as a conscientious student of this book might acquire from it. Afterwards we are ready to consider the speculations which are suggested by these facts. The facts should, of course, be presented in proper form, so that their relations may be easily recognized, and not merely enumerated as if they were totally disconnected. The opposite method is, however, much in vogue. With a very inadequate presentation of facts a mass of theoretical matter is involved, and the importance of the latter is often unduly magnified. The result is that the student, never having clearly recognized the actual connection between the facts and the speculations, and being fascinated by the various hypotheses which he has learned, but which he does not fully comprehend, makes un-

warranted use of them. We see the effects in many of the papers which appear in the chemical journals of to-day. Many of these would never have been written if the writers had ever learned to look at chemical phenomena purely objectively. I. R.

LEHRBUCH DER ORGANISCHEN CHEMIE ODER DER CHEMIE DER KOHLENSTOFFVERBINDUNGEN: von DR. AUG. KEKULÉ, Professor der Chemie an der Universität zu Bonn. Fortgesetzt unter Mitwirkung von DR. R. ANSCHÜTZ, Privatdocent in Bonn, und DR. G. SCHULTZ, Privatdocent in Strassburg. Dritter Band. Dritte Lieferung.

The sudden appearance of some old friend who has not been heard from for thirteen years, and who has consequently been given up for lost, could not occasion more surprise than did the unexpected appearance of a new number of Kekulé's great treatise on organic chemistry. The last number published in 1867 was the first one of the third volume; then, in 1880, came the second number. Now we have the third, and, though we cannot quite get over a feeling of uncertainty, and the fear that our erratic friend may again leave us in the lurch, it behooves us in the meantime to be thankful for what we get, and to take courage from the brief notice with which Professor Kekulé reintroduces his work. He says: "As my occupation leaves me even now very little time for literary labor, I have considered it necessary to call in younger forces, and I believe that I have found efficient coöperators in Dr. Anschütz, of Bonn, and Dr. Schultz, of Strassburg. The assistance of these gentlemen is secured for the future, so that rapid progress of the work may be promised with confidence."

This book has had a curious history in some respects. The time occupied in writing it was necessarily so great that the author changed his views regarding some important matters more than once before the end of the second volume was reached. If a student should attempt to work through it now without being fairly familiar with the history of chemistry during the past fifteen years, he would certainly be much mystified at times. This fact, however, scarcely diminishes its value. For an advanced student it is nearly as valuable to-day as the day it first appeared. The grasp of the author is shown on every page. No man without a very vigorous and broad mind could have written such a book. And no doubt it has exerted a powerful influence on the progress of chemistry. It is suggestive throughout. Much of the work which has been done in Germany during the past twelve or fifteen years owes its incentive to Kekulé's Organic Chemistry. It may be that, as Kolbe so persistently claims, a great deal of this work is bad, but it must not be forgotten that a great deal is good; and in order to get good work we must always have a fair proportion of that which is bad, no matter under what influence it is done, or what may be the guiding hypothesis.

But it is both too late and too early to pass judgment on Kekulé's book as a whole. Too late, if the intention is merely to call attention to it, for every chemist knows it well. Too early, if the object is to determine exactly the character of the influence which it has exerted on the progress of chemistry: that must be left to the future historian of the science. It is, however, justifiable to express a doubt whether the parts of the book which are still to appear will come up to the standard of the old parts. This depends to a great extent upon the amount of editorial work which the nominal author does upon it. It is possible to conceive of such a division of labor between Professor Kekulé and his co-workers that all the matter collected should be digested by the chief and then presented by him after it had undergone this process. We might under such circumstances get a product which would be worthy of Professor Kekulé. But, as he himself says in his brief introductory note, he has very little time for literary labor, so that plainly the ideal arrangement is an impossibility. What we shall probably get will be a very excellent handbook of organic chemistry, accurate in details and presented in clear form; but this will not be a continuation of *Kekulé's* book. Kekulé will be left out; and it was after all the Kekulé in it that made it so valuable and so popular. The prophecy may be somewhat premature, but an examination of the numbers at hand seems to justify it.

I. R.

Report on Progress in Physiological Chemistry.

[*Continued from page 366.*]

Gastric Digestion and the Products formed.

Chemical Nature of Peptones.—Although there has been, particularly of late, considerable work done upon this important subject, it has not as yet led to a complete agreement of opinion. In fact, the numerous results which have been recorded within the last five years have been so strikingly at variance with each other, that the theories of the chemical nature of peptones have been from time to time variously modified. This is probably in part explained by the great diversity of conditions under which the experiments have been conducted; conditions which, though slight in themselves, no doubt play an important part in determining the nature and composition of the products formed. Thus Herth calls attention, in the artificial preparation of peptones, to the fact that by long-continued digestion the products formed are liable to differ somewhat from those obtained in the case of rapid digestion (4–6 hours), and speaks in favor of the latter method as more analogous to what takes place in the body normally. The difficulty attending the preparation of a chemically pure peptone

by artificial digestion is more dependent upon the great liability of not completely removing syntonin than upon the presence of fats and other possible extractives. The removal of syntonin from a digestive fluid, by neutralization of the acid, offers two difficulties: first, the propensity of the peptones to form with different metals salt-like combinations which, unfortunately, are not constant in composition, as is noticeably the case when solutions of calcium or barium hydroxides are used for the neutralization of the acid; and, secondly, the difficulty of obtaining a *complete* neutralization when sodium carbonate is used, which, while it diminishes the inorganic impurities of the peptones, renders extremely difficult the complete removal of the unaltered albumin. When, however, from the method of preparation, barium or calcium chloride is present in the peptones, recourse is generally had to repeated precipitation and digestion with alcohol, which, however, fails to completely remove the salts. Again, it has been suggested to separate the baryta from peptones by careful addition of sulphuric acid, the liberated hydrochloric acid being removed in its turn by moist silver oxide, a method, however, which does not yield uniform results, owing probably to the oxidizing action of the silver oxide.

In the preparation of pure peptone, Herth,[1] who worked under the guidance of Maly of Graz, employs phosphoric acid, which, according to Gorup-Besanez, works only one-tenth as actively as hydrochloric acid. For proteid material he uses coagulated albumin from fresh eggs, and as ferment a pepsin solution made according to the method of Krasilnikoff[2] and Brücke, and purified by dialysis. The method, which is detailed as follows, is characteristic of the means adopted by many workers on this subject to obtain chemically pure products without reference to the physiological conditions normally present in the digestive process: Coagulated albumin from sixty eggs is digested for 24 hours in 1 per cent. phosphoric acid for the complete removal of inorganic salts, then thoroughly pressed and finally extracted with boiling water; the purified product is then heated at 40° C. with 4 litres of .65 per cent. phosphoric acid, to which 40 cc. of the clear pepsin solution have been added. At the end of five hours the entire mass of albumin is almost completely dissolved, although the digestions are usually continued somewhat longer. When the digestions are finished the phosphoric acid and syntonin are removed by the addition of freshly-precipitated and thoroughly-washed lead carbonate; this being added until the clear yellow fluid shows itself exactly neutral to litmus. The small quantity of lead contained in the filtrate is removed by hydrogen sulphide. The fluid is then concentrated on the water-bath and finally precipitated with strong alcohol. The so-prepared peptones are digested with alcohol, finally dissolved and reprecipitated, this operation being repeated three times.

[1] Robert Herth, Zeitschrift f. physiolog. Chem. 1, 277.
[2] Krasilnikoff: Hoppe-Seyler's med. chem. Untersuch. p. 241, 1867.

Peptones prepared in this manner are pure white; heated over sulphuric acid for several hours at 100° C. they lose from 4 to 6 per cent. of water, and at this temperature become brown in color. Their aqueous solutions react exactly neutral, and in every other respect their reactions agree with those noticed by other late observers. Particularly noticeable was the unlimited solubility of the peptones in water, which character was not changed by long soaking in alcohol, nor even by long-continued boiling in alcohol.

By a study of the reactions of his peptones with different precipitants, Herth disagrees with Adamkiewicz[1] when he says that "peptones possess the same precipitability with the important chemical reagents as albumin." According to Herth, the peptones do form, even with the heavy metals, the same compounds as albumin, most of which, however, are soluble, while the albumin compounds are insoluble. For analysis the peptones were dried at 100–105° C. till of constant weight. A portion dried at 100° C. in an atmosphere of hydrogen showed no essential difference on analysis.

	Albumin. (Wurtz.)	Albumin peptone. (Herth.)	Fibrin. (Maly.)[3]	Fibrin peptone. (Maly.)
C	52.9	52.60	52.51	51.40
H	7.2	7.12	6.98	6.95
N	15.7	16.80	17.34	17.13
Ash		1.00		

Taking the analysis of albumin by Wurtz as an average result, although the nitrogen is undoubtedly too low from the method of determination, it is seen that there is but little difference in composition between the albumin and the peptone formed from it. On the other hand, there is a noticeable difference in composition between the albumin-peptone of Herth and the fibrin-peptone of Maly.

Herth has also made a large number of analyses of peptones prepared by fractional precipitation with alcohol and ether, and, from his closely-agreeing results, decides on the individuality of the peptones, and that there are no grounds for belief in the theory of peptones being a mixture of several closely-related bodies, as has been sometimes suggested.

Adamkiewicz[1] concludes from his study of peptones that chemically they are nothing but albuminates, which differ from ordinary albumin by containing a diminished content of inorganic salts and a somewhat different molecular formation. Adamkiewicz's view is mainly based on Lehman's analysis of blood-fibrin, which contained 2.17 per cent. of ash. This theory has been contradicted by various authorities, particularly by Maly and Herth, both of whom found the quantity of salts only slightly, if at all, dimin-

[1] Die Natur und der Nährwerth des Peptons, 1877.
[2] De la Nature et du Role physiologique des Peptones, 1878.
[3] Pflügers Archiv. **20**, 329. [4] *Loc. cit.*

ished when pure albumin was employed in the preparation of the peptone. Again, Kistiakowsky[1] has found only .65 per cent. of ash in pure fibrin, while Adamkiewicz's peptones contain 1.16 per cent. of ash. Undoubtedly the quantity of salt is simply dependent upon the manner of preparation of the peptone; the purer we obtain the albumin or peptone the freer it is from ash. But perhaps the most striking proof of the falsity of Adamkiewicz's views is shown by Aronstein's oft-quoted experiments. He found that while albumin, deprived of its salts, was as non-coagulable by heat as a solution of peptones, addition of salts to such a solution of albumin restored its coagulability, while the peptone solution under like treatment was unaltered. Thus the most striking feature of peptones, viz. their non-coagulability, is wholly independent of inorganic salts.

Herth concludes that the analytical data give no idea of the actual alterations which albumin undergoes in its transformation into peptone, and thinks it possible that a rearrangement of the atoms takes place, a different grouping in the albumin molecule through the process of peptone formation. The belief in the possibility of an inner alteration of the albumin with a simplifying of the molecule, whereby, as in the case of peptone, a greater solubility, diffusibility, etc., are obtained without changing the percentage composition, has had but few supporters. Herth, however, quotes in favor of this view the fact that paraldehyde $(CH_2O)_3$, which, in the ordinary condition is solid and insoluble in water, is volatilized by heat, and shows a vapor-density agreeing with the formula CH_2O, ordinary aldehyde; even heating with water is sufficient in some cases to bring about a decomposition of complicated molecules, thereby leading to solubility in water exactly as in the case of heating albumin with water. Thus Herth is inclined to compare the change of albumin to a disgregation of the molecular compounds, or, in other words, to look upon the formation of peptones as the simple solution of polymeric bodies.

In opposition to the theory of Adamkiewicz and that of Herth, Henninger[2] has, in a long and able investigation, studied the properties and composition of various peptones, compared the results with the composition of the original proteid, and advanced the theory advocated by Wurtz and Hoppe-Seyler, that the formation of peptones is due to a process of hydration. The following figures represent his average analytical results:

	Fibrin peptone. (Henninger.)	Fibrin. (Maly.)	Albumin peptone. (Henninger.)	Albumin. (Wurtz.)	Casein peptone. (Henninger.)	Casein. (Dumas & Cahours.)
C	51.58	52.51	52.31	52.90	52.13	53.50
H	7.02	6.98	7.05	7.20	6.98	7.05
N	16.66	17.34	16.38	15.70	16.14	15.77
Ash	0.31	...	0.51	...	1.15	...

[1] Pflügers Archiv. 9, 438. [2] De la Nature et du Role physiologique des Peptones, 1878.

It is evident from these analyses, which do not differ materially from those of Maly and Herth, that the peptones, while they approach in composition the original proteid, contain regularly a diminished amount of carbon (0.5–1 per cent.), a difference altogether beyond the errors of analysis. Hydrogen and nitrogen, however, are not materially different in the two classes of compounds, a fact which is easily reconciled with the theory of hydration which Henninger adopts as the true explanation of the formation of peptones. The formula of albumin established by Lieberkühn is $C_{72}H_{112}N_{18}O_{22}S$, which would give to albumin the molecular weight of 1612. Supposing, now, the formation of peptones to be a simple process of hydration, the addition of one molecule of water, viz. 18, would increase the percentage amount of hydrogen only to a very insignificant extent, about .05. On the other hand, the content of carbon would be diminished in the neighborhood of .5 per cent., while that of nitrogen would be decreased .18 per cent. It thus becomes very apparent that the elementary analysis of peptones cannot be expected by itself to absolutely prove the hydration hypothesis. Adopting the results of Schützenberger's[1] late work on the constitution of albumin, and assuming 4800 to represent more correctly the molecular weight, a diminution of 1 per cent. in the proportion of carbon would suppose an addition of six molecules of water in the process of hydration. Thus, while the analytical data tend to corroborate the hydration hypothesis as the true explanation of the transformation of proteid matter into peptones, many other facts tend to make this the more plausible theory; for we well know that peptones are formed under the influence of agents which produce hydration; thus, boiling water, the action of dilute acids, and lastly ferments, the nature of which is to decompose by hydration; all of which facts tend to substantiate the hydration theory.

Not satisfied with this, however, Henninger[2] has attempted to produce albumin again from his peptones by a process of *dehydration*. This he partially succeeded in doing, by heating a mixture of 10 parts of dry peptones with 25 parts of glacial acetic acid at 80°C. for one hour. The acid fluid was then distilled until the greater part of the acid was removed. The residue was dissolved in a little water, and subjected to dialysis for the complete removal of the acid. The clear solution remaining possessed the following characters:

1. It is coagulated by heat, the precipitate being insoluble in a small quantity of nitric acid.

2. It gives, with nitric acid, a white precipitate, soluble in a large excess.

3. It is completely precipitated by acetic acid and potassium ferrocyanide.

4. It is completely precipitated by careful addition of potassium hydroxide, the precipitate being redissolved by a slight excess.

[1]This Journal, 2, 207-210. [2]*Loc. cit.* p. 53.

5. It is precipitated by solutions of the neutral salts, sodium sulphate, potassium nitrate, etc., the precipitates being readily dissolved by an excess of acetic acid.

It is thus very evident that the product formed is syntonin, the next modification of albumin.

This very important result has received confirmation from Hofmeister,[1] who, working on gelatin, discovered that pure gelatin, by repeated drying at 130°C., passes completely into a substance which possesses all the chemical properties of collagen. Led by this reaction, he tried a similar experiment with peptones, and obtained a corresponding result. If dried fibrin-peptone is heated for several hours at 140°C., or a shorter time at 160-170°C., it becomes changed in part, under browning and evolution of alkaline vapors, into a substance similar to albumin. Cold water dissolves a great part of the substance, while a flocculent residue remains which shows all the reactions of freshly precipitated albumin. This, then, seems to establish on a firm basis the theory that peptones are simply proteid bodies modified by hydration. Kossel[2] has analyzed the chlorine- and calcium compounds of fibrin-peptones, and has found the free peptones to possess a somewhat different composition from that already stated. His results, calculated for the free peptones, are as follows:

C	H	N	S	O
48.97	7.06	15.14	1.16	27.67

These results, which differ widely from those of Maly,[3] Henninger and others, can be explained according to the views of the author in several ways: first, the free peptones when dried at 110° C. possibly give up water which exists in chemical combination, while the peptone compounds retain it when dried at the same temperature. Maly[4] however looks upon the inorganic constituents of Kossel's peptone compound (2.34 per cent. chlorine and 5.68 per cent. calcium) as mere impurities, though Kossel purified his product by repeated precipitation with alcohol, in which free calcium chloride is readily soluble. Maly then argues that if such is the fact, the average composition of Kossel's peptone would be changed to C51.51.H7.13 and N15.95 per cent. which indeed does not materially differ from the results of Maly, Henninger and others. Again, it is possible that the compounds analyzed by Kossel are the results of a further hydration, whereby compounds with a smaller content of carbon would naturally be formed. This seems the more probable, since the peptones of Maly and Henninger particularly were the products of a weak digestive action, while those of Kossel were formed by 24 hours' digestion at 38° C., with an active gastric juice containing .4 per cent. fuming hydrochloric acid.

[1] Zeitschrift f. physiolog. Chem. **2**, 206.
[2] Zeitschrift f. physiolog. Chem. **3**, 58. Pflügers Archiv. **13**, 309.
[3] Pflügers Archiv. **9**, 585; **20**, 315.
[4] Pflügers Archiv. **20**, 325.

These results again suggest the possibility that peptones are a mixture of several isomorphous bodies. Maly[1] holds to the opinion that there is only *one* principal product of digestion, only one peptone, which differs but slightly from the mother-substance in composition, and that, therefore, peptones are not a product of the *splitting-up* of albumin. Kossel, however, finds in his work evidence that the composition of the peptone is in part dependent on the activity of the pepsin digestion, the product first formed being by further hydration changed to another body of somewhat different composition. Thus Kossel is inclined to the belief that more than one peptone can originate from a single albumin, and that those bodies which we now term peptones do not actually possess a chemical individuality. This view would accord with Kühne's[2] discoveries in regard to the two kinds of peptones, which he distinguished by the names *hemi-* and *anti-*; and although no chemical analysis has yet been made of these two bodies, which differ so far as is known only in their behavior to trypsin, still it is more than probable that two bodies which differ so widely in their mode of decomposition differ also more or less in composition. Again, Kossel[3] well remarks that if only one peptone is formed by digestion, in fractional precipitation, the more soluble portion would not differ in composition from the remaining fractions. A study of the composition of Maly's[4] fractional alcohol precipitates indicates that his product is a mixture of several bodies. Herth's results,[5] obtained by fractional lead precipitations, would seem to indicate the same thing, viz. that from albumin several bodies originate; but this result must be accepted with some modification, as it has been shown that the lead acetate is capable of working a decomposition. By a comparison of Maly's and Kossel's preparations it is noticeable, as regards the percentage of carbon, that under Maly's figures are differences which are greater than the difference between his lowest figure and Kossel's highest.

Maly's		Kossel's	
3d fraction.	2d fraction.	2d fraction.	1st fraction.
52.33	50.80	49.69	48.98
1.53	1.11	0.71	

As regards the nature of peptone, whether it is an acid, base, or both, the preponderance of evidence is on the side of its being an acid, though capable of acting both as an acid and a base. Lehman originally ascribed to peptones acid properties. Recently, however, Kossel has formed combinations of peptones with acids. This view of the acid character of peptone has also been confirmed by Henninger,[6] who likewise prepared compounds of peptone with sulphuric, hydrochloric and nitric acids. He considers them as feeble amido-acids, and as such are capable of acting either as

[1] *Loc. cit.*
[2] This Journal, **2**, 210.
[3] Pflügers Archiv. **21**, 183.
[4] Pflügers Archiv. **9**, 585.
[5] Zeitschrift f. physiolog. Chem. **1**, 289.
[6] *Loc. cit.* 43-44, also Comptes rendu, **86**, 1415.

acids or bases. Thus by the addition of baryta water to an aqueous solution of peptone, an alkaline solution is obtained, from which carbonic acid will precipitate a portion of the base, while barium *peptonate* remains in solution and can be precipitated by alcohol.

The combination of peptone with acids is formed directly whenever an acid is added to a solution of peptone. Thus if peptones are dissolved in glacial acetic acid, and then sulphuric, nitric or hydrochloric acid be added, an abundant white precipitate is immediately formed, which settles at once as a viscous mass to the bottom of the dish. This compound is a salt of the peptone corresponding to the acid employed. It is entirely soluble in water, yielding a colorless solution. Peptones also combine with salts, such as calcium chloride, phosphates, etc., all of which are insoluble in alcohol. By dialysis the greater part of the salt is removed, as its osmotic power is greater than that of the peptone itself. This fact well illustrates the loose union existing between the peptone and the salt.

Propeptone.—When fibrin is subjected to pepsin digestion, several bodies other than true peptones are formed. Among these is one which of late has attracted considerable attention. Several years ago Kühne called attention to a peculiar albuminous body formed during digestion, which he named hemialbumose.[1] Since then Schmidt-Mülheim[2] has written considerable concerning a body which he terms propeptone, evidently identical with Kühne's hemialbumose. Recently Salkowski[3] has called attention to the fact that when fibrin is digested with pepsin for a few hours only, a solution is obtained which, on neutralization and concentration, gives the well-known reactions with acetic acid and potassium ferrocyanide, with acetic acid and sodium chloride, and with nitric acid, indicating the presence of what Meissner terms a-peptones. All three of these reactions, however, disappear on heating, but return again as the solutions become cool. The reactions, then, are not due to albumin, for this must necessarily be precipitated by heat. When such a gastric digestion is continued for 1–2 days, then these reactions are not obtained; the intermediate product has been wholly transformed into peptone proper. This fact may perhaps throw some light on the difference in composition noticed between peptones which result from a long-continued and active digestion, and those which are formed by shorter digestions with weaker but perhaps purer digestive fluids. This intermediate pro-

References to other recent investigations on the chemical nature of peptones:—C. A. Peckelharing: Zur Kenntniss des Peptones, Pflügers Archiv. **22**, 185. A contradiction by Maly of a portion of this investigator's work is contained in Jahresbericht d. Thierchemie für 1880, 31. A. Danilewsky: Ueber den Hydrationsvorgang bei der Peptonisation. Centralbl. f. d. med. Wiss. 1880, **42**. Weiteres über das Peptone. C. A. Peckelharing, Pflügers Archiv. **26**, 515, 1882.

[1] This Journal, **2**. 211.

[2] Zur Richtigstellung der Geschichte Propeptons, Virchow's Archiv. **81**, 575. Weitere Beiträge zur Kenntniss des Propeptons, Jahresber. d. Thierchemie für 1880, 23.

[3] E. Salkowski, Virchow's Archiv. **81**, 552.

duct, which Salkowski recognizes as Kühne's hemialbumose, can be prepared in some quantity as follows: 50 grams of commercial *peptonum siccum* are poured into 500 cc. 1 per cent. sodium chloride solution, and heated on the water-bath. The slightly turbid fluid is then acidified with acetic acid and boiled, whereby some albumin is generally precipitated. The filtrate, after cooling, is treated with powdered salt in sufficient quantity to have a portion remain undissolved (about 37.5 grams to 100 cc. fluid), and the mixture shaken vigorously. Almost immediately a light, somewhat tenacious precipitate settles out, which is washed with salt solution. The pressed precipitate is then dissolved in 300 cc. warm water, when the proteid body is again precipitated by the addition of an excess of salt to the strongly acidified solution. This second precipitate of hemialbumose, with considerable salt, is then dialyzed until the outer fluid gives only a slight or no reaction with silver nitrate. The filtered inner fluid is then concentrated, and the hemialbumose precipitated by the addition of an excess of absolute alcohol.

The so-prepared substance is a snow-white powder, free from ash and soluble in warm water. A 5 per cent. solution shows the following characteristic reactions:

1. Heated to boiling, it is not coagulated.

2. Pure nitric acid gives a precipitate which, by warming, dissolves with an intense yellow color. The precipitate reappears on cooling.

3. It gives precipitates with acetic acid and potassium ferrocyanide, with Millon's reagent, and yields the biuret reaction.

The substance rotates the plane of polarized light to the left, a 5 per cent. solution having for white light a specific rotary power of 78–80°. When heated at 140° for 14 hours the hemialbumose becomes insoluble, hardly dissolving at all even in boiling water.

It thus becomes plain that in an artificial as well as in a physiological pepsin digestion at least three well-defined products can be separated: 1. The so-called neutralization precipitate, syntonin or antialbumose[1] of Kühne; 2. Hemialbumose or propeptone precipitated by sodium chloride; 3. Peptone proper or true peptones, including both the hemi- and antipeptones of Kühne. In a long-continued or very active digestion, the first and second products are further changed into the true peptones. Thus it is more than probable that in many cases products which have been studied as true peptones, notably in the case of Adamkiewicz, have been in reality a mixture of these three bodies in varying proportions depending on the activity of the digestive fluid. It yet remains to be proved whether the so-called true peptone is a mixture or a chemical individual, for at present there is not sufficient evidence to warrant a decisive conclusion. Undoubtedly the true peptones

[1] See this Journal, 2, 211.

may undergo further hydration or partial decomposition by long-continued digestion, since it is well known that the pancreatic ferment changes a part of its peptones into crystalline decomposition products. It would not be strange then if gastric peptones, even though they possess at some period in their formation a chemical individuality, should by further digestion undergo a partial decomposition.

R. H. CHITTENDEN.

(To be continued.)

THE RELATIONS BETWEEN THE PHYSICAL PROPERTIES OF ORGANIC BODIES AND THEIR CHEMICAL CONSTITUTION.

Under this title J. W. BRÜHL gives an account of a large number of observations recently made by him, the object of which was to show what relation, if any, exists between the chemical constitution and the thermal phenomena of liquid carbon compounds. The full memoir has appeared in volume II of the *Monatshefte für Chemie*, p. 716. The author has, however, furnished a good abstract which is published in the *Berichte der deutschen chemischen Gesellschaft*, 14, 2533, and from this the following account is mainly taken.

The previous investigations[1] of the author have shown that a simple relation exists between the refractive power and the constitution of liquid carbon compounds. It has also been found that simple relations exist between the constitution and the density, the boiling point, the rate of transpiration, and probably also of the specific volume. To use his own words: "This correlation of the various physical manifestations of organic compounds induced me to compare also their thermal and optical properties with each other, and led me to the discovery of a very simple connection between the refractive power and the heat of combustion of these bodies.

"I. It was first found that, if oxidation of the bodies be effected in successive stages, the changes exert the same influence on the optical as on the thermal properties. The refractive power $\frac{A-1}{d}$ of a body is decreased as the body unites with more and more oxygen; the more oxygen enters into the compound, the less the refractive power becomes, just as the heat of combustion is also decreased by this process. The abstraction of hydrogen or the replacement by oxygen produces the same result, so that the refractive power as well as the heat of combustion of the hydrocarbons is greater than that of equal weights of all the bodies which are formed by oxidation of the hydrocarbons, as the corresponding alcohols, aldehydes,

[1] This Journal, 2, 352.

acids, oxyacids, etc. The differences between the thermal and optical constants of adjoining members of an oxidation series decrease with increasing molecular weight, when the bodies have analogous structures. Thus these differences are smaller between propyl alcohol and propyl aldehyde, than between ethyl alcohol and acetic aldehyde, etc.

"II. The influence of the introduction of the halogens in the optical and thermal constants is analogous to that of oxidation. The specific refractive power and the specific heat of combustion, *i. e.* that of equal weights of the bodies, become the smaller the more chlorine atoms enter. . . .

"III. In the homologous series of alcohols, acids and esters, the refractive power and the heat of combustion increase as the number of carbon atoms increases, while the differences for the increment CH_2 decrease with increasing molecular weight in the case of both constants.

"IV. I had previously proved that the refractive power of isomeric bodies of the same degree of saturation is the same, and hence independent of the structure. Substances of one and the same class, and the same molecular formula, as, for example, isomeric alcohols, aldehydes, acids, etc., are hence, as regards their optical properties, identical. The latest investigations of Louguinine, Berthelot and others have shown that isomeric bodies of analogous chemical character evolve the same quantities of heat when burned.

"V. The relation between the refractive power and the heat of combustion holds good also for polymeric substances. The constants of the polymerisation products are in both cases smaller than those of the mother-substances. . . .

"VI. Isomeric bodies of unequal degrees of saturation have unequal refractive power. I proved that bodies which contain doubly linked atoms have greater refractive power than isomeric bodies in which this kind of linking does not occur. It was shown further, that the refractive power of such bodies as contain doubly linked carbon atoms is greater than that of bodies which contain carbon and oxygen doubly linked together. The general correlation in the optical and thermal conduct of bodies made it appear probable that the influence of double linkage of the atoms would extend to the heat of combustion of the bodies. This assumption is confirmed by the latest observations of Louguinine.

"These showed, first, that the heat of combustion of bodies in which doubly linked carbon atoms occur is greater than that of isomeric bodies, in which this kind of linkage is not found, but in which double linkage of oxygen and carbon is present.

"Thus the unsaturated alcohols evolve more heat than the isomeric aldehydes or ketones, and this accords with the optical conduct of these bodies. Allyl alcohol, for example, whose refractive power is greater than that of propyl aldehyde and of acetone, also evolves more heat when burned than these substances.

"VII. The phenomenon, that the double linkage of atoms which increases the refractive power of bodies, also increases their heat of combustion, throws light on the nature of this kind of atomic union.

"When two substances of the same molecular formula evolve unequal quantities of heat on combustion, the cause can only lie in the different energy of these compounds. Hence by the above results we are led to the conclusion that the energy of substances in which double linkage of atoms occurs is greater than the energy of isomeric substances in which such double linkage is lacking."

The fact that the unsaturated compounds have greater energy than the saturated, indicates that the atoms are not as intimately associated in them as in the saturated compounds; or, to state the conclusion in the author's words: "*It follows that the so-called double linkage of atoms in reality represents not a stronger, but a weaker attraction than the simple linkage. The assumption of a stronger or closer union of the atoms, of a double linkage between them, in unsaturated bodies, is hence in direct opposition to facts.*"

"This result is also partly confirmed by investigations on the specific volume. The well-known labors of Kopp and of Buff showed that the supposed doubly linked atoms require more space than those that are singly linked. This is easily understood if, in accordance with the above reasoning, we assume that the so-called double union does not correspond to a more intimate, but rather to a weaker connection of the atoms. For it appears then quite natural that the specific volume of atoms should be greater, *i. e.* that they should be farther removed from each other, the more loosely they are connected. If, however, we assume, as heretofore, that the unsaturated atoms are more intimately or doubly united, it is not clear why they should be farther removed from each other than those which are more weakly or singly united.

"This reasoning finds farther support in the rule discovered by Kekulé that in the oxidation of bodies with so-called double linkage of carbon atoms, the splitting of the molecule takes place just where this double linking is supposed to exist.

"The greater 'disgregation' of unsaturated compounds, and the fact that their molecules occupy relatively greater space, may be indicated in their structural formulas by representing the distance between unsaturated atoms as greater than that between the saturated. Thus, for example, we might express the connection of the atoms in allyl alcohol and propyl aldehyde by the following formulas:

$CH_2 \ldots CH\text{–}CH_2.OH$	$CH_3\text{–}CH_2\text{–}CH \ldots O.$
Allyl alcohol.	Propyl aldehyde."

On the Specific Viscosity of Liquids and its Relation to their Chemical Constitution.

Graham several years ago recognized that a connection exists between the chemical constitution of various liquids and the time of their transpiration through capillary tubes. Rellstab and Guerout subsequently investigated several liquids with reference to this property. The most thorough investigation of the subject has recently been made by Richard Pribram and Al. Handl. The capillary tube, which contained the liquid examined, was immersed in a larger tube filled with water, kept at a constant temperature. The authors employ for the specific viscosity (Zähigkeit) the expression

$$z = \frac{t.\ 100}{t_\omega},$$

where t represents the time of transpiration of the liquid considered, and t_ω the time of transpiration of an equal volume of water through the same capillary tube.

It was proved by earlier investigators that in homologous series the time of transpiration of liquids increases with the molecular weights. The more recent results of Pribram and Handl confirm this conclusion, and show further that in homologous series the specific viscosity of liquids, at elevated temperatures, increases by a constant. The following tables contain the specific viscosity of three classes of homologous liquids as determined by them :

	Z. 50°C.		Difference.
Isoprophyl chloride	16		
Isobutyl "	19	...	3
Issamyl "	22	...	3
Nitroethane	29		
Normalnitropropane	34.5	...	5.5
Normalnitrobutane	39	...	4.5
Propionic acid	45		
Normalbutyric acid	57	...	12
Valeric acid	71.5	...	14.5

In aldehydes and ketones, compounds which contain dissimilar atoms joined by double union, the specific viscosity is considerably less than in the corresponding alcohols where single union prevails. A single example will make this evident :

	Z. 10°C		Difference.
Propylalcohol	175		
Propylaldehyde	26.5	.	148.5

No generalization is made concerning the effect of double union between carbon atoms upon the specific viscosity of organic compounds. In some instances unsaturated compounds, that is, compounds in which double union is supposed to exist, have a lower specific viscosity than the corresponding saturated compounds; while the reverse is frequently the case.

Guerout, relying upon his observations, stated that isomeric esters have the same time of transpiration for equal volumes. Pribram and Handl have determined the specific viscosity of a large number of isomeric esters. Their results show that Guerout's statement is wrong. From the compounds examined by them, "the ester containing the normal radical shows a greater viscosity than the ester isomeric with it, and this holds true whether the isomerism occurs in the acid or alcohol radical." This is equally true of the aldehydes, propyl alcohol (at 50°), nitropropanes, butyric acids and butyric iodides.—(*Sitzungsberichte der Wiener Akademie der Wissenschaften*, **78**, 52; **80**, 17; and *Monatshefte für Chemie*, 1881, 643.)

C. P.

NOTES.

Concerning Morphine.

The only facts hitherto known concerning the constitution of morphine, $C_{17}H_{19}NO_3$, are that, of the three oxygen atoms contained in it, two are associated with hydrogen, forming two hydroxyl groups, and the third is a "bridging" or ketone oxygen atom. It has also been considered that morphine contains a pyridine nucleus, for by distillation with caustic potassa a small quantity of pyridine was obtained. E. v. Gerichten and Hugo Schrötter have recently subjected morphine to distillation with zinc dust. In addition to the usual products, the distillate contained the hydrocarbon phenanthrene and a base which is believed to be phenanthrene-chinoline ($C_{17}H_{11}N$). The quantity of the base obtained was, however, insufficient for its thorough examination, but it seems highly probable that morphine is a derivative of phenanthrene, to which phenanthrene-chinoline is probably very closely related.—(*Annalen der Chemie*, **210**, 396.)

On New Elements and their Position in the Natural System.

D. Mendelejeff has recently published some remarks of interest, an abstract of which is given in the *Berichte der deutschen chemischen Gesellschaft*, **14**, 2821. A translation of the abstract is here given.

Of the many newly discovered metals of cerite and gadolinite, only two in addition to the well-known cerium, lanthanun, didymium

and yttrium, can be regarded as established elements. These are scandium and ytterbium. As scandium corresponds perfectly to the ekabor the discovery of which was foretold by Mendelejeff, its position in the periodic system of the elements was also determined before its discovery. Ytterbium finds a place in accordance with its properties, if the atomic weight of Nilson, 173, be accepted, and the oxide be represented by the formula Y_2O_3.

Mendelejeff gives the periodic system of the elements the following form, which he has adopted in the fourth edition of his *Principles of Chemistry*, now appearing:

			I.	II.	III.	IV.	V.	VI.
R_2O	I		Li 7	K 39	Rb 85	Cs 133	..	..
RO	II		Be 9	Ca 40	Sr 87	Ba 137	..	..
R_2O_3	III		B 11	Sc 44	Y 89	La 138	Yb 173	..
RO_2	IV	(H_4C)	C 12	Ti 48	Zr 90	Ce 142	..	Th 231
R_2O_5	V	(H_3N)	N 14	V 51	Nb 94	Di 146	Ta 182	..
RO_3	VI	(H_2O)	O 16	Cr 52	Mo 96	..	W 184	U 240
R_2O_7	VII	(HF)	F 19	Mn 55	..	..	..	..
RO_4				Fe 56	Ru 103	..	Os ?192	..
	VIII			Co 58	Rh 104	..	Ir 193	..
				Ni 59	Pd 106	..	Pt 195	..
R_2O	I	H 1	Na 23	Cu 63	Ag 108	..	Au 196	..
RO	II		Mg 24	Zn 65	Cd 112	..	Hg 200	..
R_2O_3	III		Al 27	Ga 69	In 113	..	Tl 204	..
RO_2	IV	(H_4R)	Si 28	?? 72	Sn 118	..	Pb 206	..
R_2O_5	V	(H_3R)	P 31	As 75	Sb 120	..	Bi 209	..
RO_3	VI	(H_2R)	S 32	Se 79	Te ?125	..	..	..
R_2O_7	VII	(HR)	Cl 35.5	Br 80	I 127	..	..	..

All the more carefully investigated cerite and gadolinite metals find appropriate places in the system, and there is at present no good reason for changing it as Nilson and Petterson desire to. Using this system as a guide we can, for example, predict the existence of ekamanganese, whose atomic weight will be about 100, and which will yield colored compounds and a whole series of oxides corresponding to the oxides of manganese. The changes in the atomic weights of cerium, yttrium and other elements, proposed by Mendelejeff in 1870, on the basis of his periodic law, have been shown by later investigations to be justified. The position of beryllium cannot be changed to the third or fourth group, as the decrease in the atomic heat in the series Li, Be, B, C is analogous to that in the series Na, Mg, Al, Si. The three following important conditions appear not to have been sufficiently considered in the examination of the cerite and gadolinite metals: 1. The investigation of the higher oxides, particularly in the presence of alkalies and energetic oxidizing agents; 2. the possible existence of basic salts; 3. the possibility of the formation of meta-compounds the existence of which in the case of thorium has been proved.

Nicotinic Acid from Pyridine.

Laiblin has recently shown that nicotinic acid is a derivative of pyridine, the two being related the same as benzene and benzoic acid. He tried to prepare the acid from pyridine by means of ethyl chlorcarbonate, but did not succeed. O. FISCHER has now by another method passed from pyridine to nicotinic acid. He first made a pyridinesulphonic acid by heating with pure concentrated sulphuric acid for a long time at 320–330°. The sodium salt of the sulphonic acid was then distilled with potassium cyanide, and the cyanide thus obtained treated with hydrochloric acid at 110–120°. The acid obtained was found to be identical with nicotinic acid.—(*Ber. deutsch. chem. Gesell.* **15**, 62.)

Caesium and Rubidium.

CARL SETTERBERG has made a careful study of some new caesium and rubidium compounds, and has succeeded in preparing metallic caesium from the chloride by means of electrolysis. The material was obtained by working up residues from the preparation of lithium compounds from lepidolite. Tons of this material were at his disposal. The separation of pure salts was effected as follows: Three to four hundredweight of the impure alums (the residues just mentioned) were dissolved in enough water to make a solution of 20° *Beaumé* when boiling. The deposit from this solution contains all the rubidium and caesium compounds. This operation is repeated until the potassium alum is removed. Then the crystallization is continued and rubidium alum obtained in pure condition. Finally, the caesium alum is obtained. Thinking that possibly other alkaline metals might be contained in the mixture, the crystallization of the caesium alum was continued until only a very small quantity remained. No evidence of the presence of new metals was obtained. The author prepared in the course of two weeks 40 kilograms of rubidium alum and 10 kilograms of caesium alum. Rubidium was prepared by distilling, after carbonizing, 1500 kg. rubidium ditartrate, 150 kg. calcium carbonate and the necessary quantity of sugar. The operation was in every respect satisfactory. The attempt to prepare metallic caesium by reduction of the carbonate with charcoal was not successful. By electrolysis of caesium cyanide, however, the metal was obtained, though only in small quantity. It was found better to use a mixture of 4 parts caesium cyanide to 1 part barium cyanide instead of pure caesium cyanide. Caesium is very similar to the other alkali metals. It floats on water, and acts like potassium and rubidium as regards the accompanying phenomena. It takes fire quickly in the air.—(*Annalen der Chemie*, **211**, 100.)

Obituary Notes.

JOHN W. DRAPER, M. D., LL. D., Professor of Chemistry and Physiology in the University of New York, died January 4,

1882, in his 71st year. He was born in England, but came to this country at the age of 22. He took his medical degree at the University of Pennsylvania, and was appointed almost immediately to the professorship of chemistry and physiology in Hampden Sidney College, Virginia. Soon afterwards he was appointed professor in the University of New York, and remained actively connected with that institution to the time of his death. He was widely known as an investigator and writer. Many papers written by him appeared in the American Journal of Science, the Journal of the Franklin Institute, the American Journal of Medical Science, and in the London Philosophical Magazine.

JOHN STENHOUSE, a well-known English chemist, died recently at the age of 70. He studied under Thomson and Graham in Glasgow and afterwards under Liebig in Giessen. In 1851 he was appointed to the chair of chemistry in the Bartholomew Hospital, London. He suffered a stroke of paralysis and remained permanently crippled for a number of years, and his eyes became so affected that his time was necessarily spent in a dark room. Notwithstanding these great disadvantages, Stenhouse continued at intervals to prosecute his favorite researches, especially in the field of organic chemistry, until his death.

THÉOPHILE JULES PELOUZE, born February 11, 1807, in Velouze, a scholar of Gay-Lussac and an intimate friend of Liebig, was professor of chemistry in Paris. Together with Frémy he wrote the "Chimie générale," and published a number of important memoirs on chemical subjects. He died March 4, in Paris.

RUDOLPH BÖTTGER, born in 1806, teacher of chemistry and physics at Frankfort, died April 29, at the age of 75. Though, like Schönbein, he never used a balance, his numerous discoveries were of the highest importance. Among the substances the discovery of which is due to him, may be mentioned gun cotton, collodion, safety matches. The latest and, for different branches of industry, extremely important discovery of Böttger's was that of nickel-plating oxidizable metals.

FRANZ VON UCHATIUS, the well-known discoverer of Uchatius steel and steel bronze, born in 1811 in Thereseinfeld, died June 5, 1881.

ETIENNE-HENRI SAINTE-CLAIRE DEVILLE, the eminent French chemist, was born at St. Thomas on the 11th of March, 1818. He came to Paris as a boy, and a love for chemistry was developed in him, particularly by the lectures of Dumas. At the age of 33 he was appointed professor in the "École normale superiéure" in Paris. To the public he is known through his investigations on the manufacturing of aluminium, while his numerous

memoirs, especially in the field of inorganic chemistry, have made his name immortal among chemists. Among his many discoveries may be mentioned nitric anhydride, boron (conjointly with Wöhler). His investigations on the phenomena of dissociation are classical. Deville also made successful experiments on the preparation of artificial gems. He died at Boulogne, July 1, 1881.

WILHELM WEITH was born in 1846 at Homburg. He was professor of chemistry in the University and the Polytechnic school at Zürich. He published a large number of papers on subjects from the field of organic chemistry. He died November 29, 1881.

ALEXANDER POPOFF, professor of chemistry in Warschau, died August 18, 1881. He is well known through a series of investigations pertaining to certain oxidation phenomena presented by organic compounds.

To the Editor of the American Chemical Journal:

SIR:—There appeared in your October number for this year a review of my Manual of Sugar Analysis, by Dr. C. Fahlberg, from which I quote: "Although caustic lime is mentioned as influencing the rotatory power of cane-sugar, it is not stated how calcium sucrate and other sucrates have to be treated in order to obtain correct results with the polariscope." I wish to point out, that in two places in the above mentioned work I have given the necessary directions for meeting this difficulty in the polariscopic test, *i. e.* by slight supersaturation of the alkali with acetic or phosphoric acids—first on page 176, and again on page 252, under the head of cane-sugar estimation in the chapter on the analysis of molasses and syrups, to which section there are also several cross-references.

Very respectfully,

Philadelphia, Dec. 27, 1881. J. H. TUCKER.

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